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REACTOR FUEL PROCESSING

A Quarterly Technical Progress Review

Prepared for DIVISION OF TECHNICAL INFORMATION, USAEC, by
STEPHEN LAWROSKI and ASSOCIATES, ARGONNE NATIONAL LABORATORY

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REACTOR FUEL PROCESSING

A REVIEW OF RECENT DEVELOPMENTS

Prepared for DIVISION OF TECHNICAL INFORMATION, USAEC,
by STEPHEN LAWROSKI and ASSOCIATES,
ARGONNE NATIONAL LABORATORY

● JAN. 1963
● VOLUME 6
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Foreword

This quarterly review of reactor fuel processing has been prepared at the request of the U. S. Atomic Energy Commission, Division of Technical Information. It is intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significant new results have been obtained. The Review does not purport to abstract all the literature published on this field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results, where given, represents the opinion of the editors of the Review, who are personnel of the Argonne National Laboratory, Chemical Engineering and Idaho Divisions. Those taking part in the preparation of this issue are J. Barghusen, L. Burris, Jr., I. G. Dillon, P. Fineman, A. A. Jonke, S. Lawroski, W. J. Mecham, D. Paige, J. Royal, W. B. Seefeldt, J. Simmons, R. K. Steunenberg, C. E. Stevenson, and R. C. Vogel. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

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Section

I

Reactor Fuel Processing

Commercial Aspects of Fuel Processing

Fuel-Processing Economics

The question of whether spent nuclear fuels should be processed in large central plants or in small plants associated with a small group of reactors has been a controversial subject for several years. A characteristic of radiochemical operations is that the cost is said to increase approximately as the 0.15 power of the plant capacity.[1] This low scaleup factor is a strong argument in favor of large plants. However, the high cost of transporting fuel to a processing site favors the concept of small, strategically located plants.

The case for small processing plants has been discussed by Slansky and McBride of the Phillips Petroleum Company in a paper at the 1962 Nuclear Congress[2] and in a recent journal publication.[3] These authors believe that several small plants should be built rather than a single large one. [A license application to build a large plant in western New York State has been filed with the Atomic Energy Commission (AEC) by Nuclear Fuel Services, Inc. (NFS).][4] Slansky and McBride indicate that two small plants built by private industry for $5 million each (as compared with $22 to $25 million estimated by NFS for a large plant) could recover all the low-enrichment fuels in the United States for the next 5 to 10 years.

The design features of the small processing plant proposed by a study group of the Phillips Petroleum Company were discussed in a previous issue of *Reactor Fuel Processing*.[5] Recent studies[3] indicate that the small plant has an inherent capacity for low-enrichment power fuels up to 0.3 metric ton of uranium per day. This would be the amount of spent fuel from nuclear power plants of about 750 Mw(e) total capacity.

The compactness of the small plant is the principal basis for its low estimated investment cost compared to the large plant. In the large plant, large equipment is segregated in separate cells for ready repair by remote techniques without the need for emptying and cleaning the entire plant. In contrast the unitized aspect of the small plant is intended to allow one-third to one-fourth of the equipment to be removed at one time for external maintenance after certain lines are decontaminated and disconnected. Process equipment is designed to be concentrated in a single shielded cell; this concept significantly reduces expenditures for such things as shielding, ventilation, pipe galleries, corridors, and remote disconnects.

Slansky and McBride point out that, when small batches of fuel are put through a large plant on an independent job basis, the plant holdup and turn-around time raise the unit cost of processing by a large factor. This problem of handling different fuels from many different customers has confronted the Eurochemic processing facility and has reduced its planned operating time to about 150 days/year. Obviously there would be no need to make a small plant fully universal; however, by using the chop-leach head-end method, the plant could process fuel rods clad in either Zircaloy or stainless steel.

The estimated processing costs for several processing-plant proposals are compared in Table I-1. To put all the designs on a common cost basis, the authors chose a fixed annual charge of 16.9% of the capital cost as characteristic of the electricity-generating industry. The unit processing cost, as estimated by Slansky and McBride, is remarkably low for the small plant when operating at full capacity ($22 per kilogram of uranium), being only slightly higher than the estimated unit costs for the AEC Conceptual Plant and the Davison (NFS) plant. If several small-scale processing

Table I-1 SUMMARY OF COST ESTIMATES OF PROCESSING POWER-REACTOR FUELS BY VARIOUS PLANT DESIGNS[2]

Plant	Instantaneous rate, kg of U per day	Operating days per year	U^{235}, %	Burnup, Mwd/ton	Capital cost*	Fixed charge at 16.9% per year	Operating cost per year	Total annual cost	Cost per kg of U
Phillips small plant	68	270	1.5	10,000	4.00	$ 676,000	$ 617,000	$ 1,293,000	$ 71
	120	270	1.5	10,000	4.08	690,000	711,000	1,401,000	43
	272	270	1.5	10,000	4.78	806,000	826,000	1,632,000	22
Davison Chemical Div.	1,000	300	Natural	15,000	23.0	3,890,000	2,170,000	6,060,000	20
Eurochemic	350	150	≤5	10,000	20	3,400,000	(1,700,000)	5,100,000	97
	670	150	Natural	10,000	26	4,400,000	(2,000,000)	6,400,000	64
Du Pont	1,000	365	Natural	5,000	43	7,200,000	3,700,000	10,900,000	30
	10,000	365	Natural	5,000	60	10,200,000	6,200,000	16,400,000	4.5
Allis-Chalmers (CNEN)	60 (ThO_2-UO_2)			20,000					200†
AEC Conceptual Plant (USAEC Report WASH-743)	1,000	300	<3	?	20.6	3,480,000	1,936,000	5,416,000	18‡

*Millions of dollars.

†Including fuel fabrication.

‡Actual charge from USAEC Report WASH-743 will average $20 per kilogram of uranium for a large reactor.

plants were strategically located with respect to the power-generating industry, it is said that a saving in transportation cost of 0.05 to 0.15 mill/kw-hr might be credited to the processing cost. This saving would correspond to $3 to $10 per kilogram of uranium for Dresden-reactor fuel.

The fuel load is a major factor in the economics of fuel processing. From an analysis of power reactors and their fuel discharge, it appears that about 100 metric tons of uranium per year, as slightly enriched uranium dioxide fuel in stainless-steel or Zircaloy tubes, will be the fuel load for the next five years from private and government reactors in the United States. One small-scale plant is said to be capable of handling 74 metric tons of uranium per year. According to the authors, two or three small plants would provide the means for private industry to enter the business without excessive risk in a changing market and with a chance of modest but increasing profits. Furthermore, such an entrance into the processing field could provide the competitive stimulus necessary for healthy evolution of the nuclear industry.

Cost Comparison of Two Methods for Preparing Fuel for Processing

A cost comparison has recently been made by Adams and others at Oak Ridge on two different methods of head-end treatment for preparing irradiated fuels for processing.[6] The methods compared are the mechanical shear-leach process and the aqueous Sulfex decladding process. The comparison was made for a typical power fuel, consisting of stainless-steel-jacketed uranium oxide. The mechanical process, in which the fuel is chopped into short lengths and the exposed core is leached with boiling nitric acid, has been adopted for the proposed privately owned NFS plant. In the Sulfex process the stainless-steel jacket is dissolved in sulfuric acid and discarded, and the exposed core is dissolved in nitric acid.

	Sulfex	Shear-leach
Capital cost	$5,373,000	$4,096,000
Yearly operating cost:		
Without amortization	2,247,000	1,074,000
With 6.7-year amortization	3,020,000	1,695,000
Processing cost, per kilogram of uranium	3.78	2.12

This economic comparison is based on a processing rate of 800 metric tons of uranium per year and shows that both capital cost and operating cost are lower for the mechanical process.

Another important difference between the two head-end methods is in the volume and type of waste produced from the fuel cladding. The cost of handling and storing the decladding waste from the Sulfex process was estimated as $12 per kilogram of uranium processed, whereas the cost for the cladding waste from the mechanical shear process was estimated as $0.59 per kilogram of uranium processed. If the shear process is used, most of the radioactive material remains fixed in the cladding metal, greatly decreasing the possibility that radioactive nuclides will escape to the biological environment.

Criticality hazards present a much greater problem in the continuous conveying and leaching equipment of the shear-leach method than in the Sulfex batch dissolvers. In continuous equipment the possibility of concentration transients in the liquid phase due to changes in the rate of leaching of sheared and crushed fuel causes greater concern about the possibility of a nuclear excursion. A greater safety factor may therefore be needed in the design of the continuous conveying and leaching equipment to attain the degree of reliability that the simpler Sulfex batch dissolver has.

Transportation of Irradiated Fuel

By early 1963 the transportation of spent fuel from nuclear power reactors is expected to begin in appreciable volume. Several firms are offering a complete fuel-transport service including cask rental, maintenance and inspection, arrangement and supervision of transportation, and the performance of regulatory paper work.[7]

Fuel-transport service for the N.S. *Savannah* and for the Dresden nuclear plant will be provided by the Stanray Corporation. Both reactors will be serviced by the same 70-ton cask mounted on a specially designed rail car. The cask contains six fuel cavities, each cavity being capable of carrying four Dresden fuel assemblies or one N.S. *Savannah* fuel assembly. The 14-ft-high cask uses an internal water cooling system backed up by a secondary

natural-convection water system. It was learned in a private communication that the first shipment from Dresden is scheduled for February 1963.

Spent-fuel transport for the Yankee reactor will be provided by Westinghouse using a 70-ton cask designed by Edlow Lead Company. This cask has a duplicate cooling system and a standby power source. The first Yankee shipment was scheduled for around November 1962.

Fabrication of a prototype cask to be used for the Piqua, Ohio, and the Elk River, Minnesota, reactor fuel elements has been started by Knapp Mills. In this cask the conventional cooling and heat-dissipation equipment has been eliminated. Instead, Knapp Mills has developed fuel-assembly baskets capable of carrying the heat to the cask's inner shell by conduction. A special alloy of high thermal conductivity used for the baskets also includes neutron poisons for criticality control. Maximum heat-transfer efficiency is achieved by metallurgically bonding lead to the inner and outer shells of the cask. Weighing only 28 tons, the cask will carry 19 Piqua or Elk River fuel elements and is said to have the highest capacity yet achieved in terms of fuel elements per ton shipped.

Other firms offering fuel-transport services include National Lead Company, which is preparing to service the Battelle Memorial Institute research reactor, and O. G. Kelley and Company, which has built eight 70-ton casks for the Savannah River Plant (SRP) and one 60-ton cask for the Canadian AEC.[7]

Under a Euratom study[8] the Edlow Lead Company is preparing procedures for shipping spent fuel from Euratom nations to the United States for processing. The study includes planning of routes and methods of transport, definition of required regulations and documentation, and determination of the range of costs involved. Similar studies on spent-fuel shipment have been conducted under Euratom contracts by the Stanray Corporation and by the French Groupe d'Études Nucléaires Lebon–Sogei.[9] The Edlow Lead Company, in association with several European firms, has indicated that it is prepared to offer a complete service for Euratom fuel shipments. This would include the manufacture of casks for sale or lease, the transport of shipments to designated European ports, the monitoring of shipments on arrival at U. S. ports, and the supervision of port handling and rail or road transport. According to AEC, port clearances have been obtained for several U. S. seaports in preparation for forthcoming foreign shipments of spent fuel.

The AEC is attempting to develop practical criteria to govern the shipment of highly radioactive materials, such as spent fuel elements. Drop, puncture, and fire endurance tests are being conducted by several organizations, including Franklin Institute, Underwriters Laboratory, Oak Ridge, Hanford, and Savannah River. Some of the test data are under study and evaluation.[7]

In order to provide some guarantee that reactor fuel casks have a high degree of integrity to the high-impact loading that could result from a transportation accident, AEC's proposed fuel-shipping regulations specify that a cask must maintain its shielding integrity after a 15-ft fall onto a solid unyielding object. Since data on possible cask damage cannot be calculated with any degree of certainty, data are being obtained experimentally at Oak Ridge on inexpensive small-scale models and should permit scaleup to actual cask sizes. All the cask models have an inner and outer steel shell and a lead-filled annulus.[10] In these tests the casks are instrumented. Compressometers indicate the maximum deflection in the cavity at impact, and accelerometers measure the deceleration at the location on the cask where they are attached. Inertia switches that are preset to function under a certain shock load are used to check the information obtained from the accelerometers. Strain gauges measure the strain at points of interest.

Casks have been dropped in various positions and from various heights. After casks of several sizes are dropped, the data will be correlated to determine whether the results obtained from model testing can be satisfactorily scaled up to help in setting some of the important parameters in cask design.

In another study at Oak Ridge, data on the probable temperature rise due to fission-product decay heat in spent fuel elements during shipping were obtained with electrically heated fuel rods. The simulated fuel bundles studied contained 4 to 64 tubes and were heated in air-filled casks 24 in. long and either 12 or 16 in. in inside diameter. By assuming that the bulk of the heat is transferred by radiation, it was generally possible to predict the temperatures of the center pins within 20°C at pin temperatures[10] between 200 and 300°C.

Waste Disposal

In September the AEC amended the license of Nuclear Engineering Company, Inc., Pleasanton, Calif., to permit the company to bury low-level radioactive waste at an 80-acre site in the Amargosa Desert, approximately 11 miles southeast of Beatty, Nev.[11,12] This land is owned by the State of Nevada, which is leasing it to Nuclear Engineering for this purpose.

This would be the first license issued by AEC for commercial burial of radioactive waste on state-owned land. The Commission's regulations provide that persons engaging in commercial land burial of low-level wastes must do so on federal or state-owned land. This is to assure necessary long-term control of the land. Officials of the State of Nevada and Nye County, where the proposed burial site is located, have approved the proposed license.

The typical low-level waste to be buried by Nuclear Engineering includes slightly contaminated glassware, paper wipes, ashes, and laboratory paraphernalia. It does not include high-level radioactive waste. Under the proposed license, Nuclear Engineering would bury only packaged solid wastes in approved containers. The actual burial of these wastes will be made in 100- by 50-ft trenches excavated to a depth of 20 ft. Packages of solid wastes will be stacked in the trench, and there will be a minimum of 3 ft of earth covering the last layer of packages. The radiation level at the surface of the ground will be negligible because of the low radioactivity level of the materials and because of the shielding provided by the earth fill.

The Nevada facility of Nuclear Engineering will include a building with 10,000 sq ft of floor space. The building will be subdivided into an office area, laboratory area, packaged-waste-storage area, and waste-processing area. Processing and burial activities initially will be carried out in a 40,000-sq ft area of the 80-acre site. This area will be enclosed by an 8-ft-high fence.

Nuclear Engineering will have adequate radiation-detection instruments, air-sampling devices, and personnel-monitoring devices at the facility. The company has drilled a test well on the site, from which it will obtain periodic water samples to determine whether there has been any increase in radioactivity in the ground water due to burial operations.

In October this same company was licensed by the State of Kentucky to bury low-level waste at a site near Flemingsburg, Ky.[12]

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Section

II

Reactor Fuel Processing

Research and Development on Aqueous Processing

Although the principal methods for the recovery of plutonium and unused uranium from irradiated uranium fuels continue to require acid dissolution and solvent extraction, the amount of research and development work carried out on such processes is diminishing. Less work is being done on metallic fuel compositions, whereas ceramic fuels are becoming of more concern.

Culler and others[1] have recently published a useful summary of aqueous processing techniques as they might be applied to power-reactor fuels. Eight decladding and nine fuel-dissolution procedures, along with seven solvent-extraction systems, are described briefly as comprising 25 possible applications to fuels from eight typical reactors. The current development status of each of the processes is roughly indicated. It is of interest to note that only two applications have reached the status of hot demonstration on a pilot-plant scale and that complete hot-cell tests have been made for only five more.

Preparation for Fuel Processing

Fuels may be readied for separation of the desired products by disassembly and fragmentation followed by core dissolution, by chemical decladding and separate core dissolution, or by total dissolution. There has been little recent work reported on mechanical treatment.

Chemical Removal of Cladding Materials

Stainless-steel cladding may be removed from uranium dioxide pellet fuel by dissolving in dilute sulfuric acid. Oak Ridge[2] has recently reported successful hot-laboratory tests of this procedure. In 19 experiments, type 304 or 316 stainless-steel cladding was effectively dissolved in three times the stoichiometric amount of 4*M* sulfuric acid. Activation with iron wire was necessary to initiate attack by the acid. The cladding solution contained some undissolved scale and uranium dioxide fines, although losses of uranium and plutonium from pellets irradiated to between 1545 and 28,200 Mwd/ton generally were only 0.3%.

Dissolution of Fuel Cores

The dissolution of uranium in complex dissolving reagents is of significance in processing metallic fuels. Since uranium may be associated with thorium, work at Oak Ridge has included studies of dissolving uranium in thorium nitrate–nitric acid solutions.[3] The instantaneous dissolution rate of uranium metal in boiling 1.5*M* thorium nitrate containing nitric acid was found to increase from 0.31 to 15.9 mg/(cm^2)(min) as the acid concentration was increased from 0.05*M* to 4.2*M*. The rate was further increased by passing air through the solution during dissolution.

In considering the dissolution of molybdenum alloys, Faugeras and others[4] have studied the solubility of molybdic oxide in nitrate systems as a function of acidity and of iron and uranium concentrations. Solubility equilibria are only slowly attained at room temperature but are reached in a few hours at 100°C. At this temperature in nitric acid alone, a maximum solubility of about 3.5 g of molybdenum per liter was noted in 3.7*M* nitric acid, with less solubility at higher and lower acidities. Similar maxima were observed, but at lower free acidity, in both the ferric and uranyl systems. With uranyl nitrate, up to 9.6 g of molybdenum per liter was dissolved at about 1.5*M* free nitric acid, whereas ferric ion was much more

effective in solubilizing molybdenum, with up to 40 g of molybdenum retained in solution at low acidity. In the latter case the molybdenum solubility was depressed somewhat by the presence of uranium.

Dissolution of Plutonium

Plutonium metal, like thorium and unlike uranium, cannot readily be dissolved in nitric acid alone. Hydrofluoric acid is usually added to nitric acid to effect dissolution, and corrosion-resistant equipment is required. Jenkins,[5] in studying the dissolving of off-specification plutonium metal for repurification, notes that plutonium dissolves readily at room temperature in dilute sulfamic acid, both with and without added nitric acid. Sulfamic acid is relatively noncorrosive to stainless steel. In 1 hr a concentration of 134 g of plutonium per liter was achieved at 25 to 40°C in a reagent initially containing 1.7*M* sulfamic acid. At higher temperatures and in the presence of nitric acid or other oxidizing agents, sulfamic acid is decomposed and the excess sulfate yields a sludge. It is conceivable that sulfamic acid might be a useful agent to dissolve plutonium fuels for processing.

Total Dissolution of Metallic Fuels

The laboratory development of a nitric-hydrochloric acid dissolution-TBP extraction process for a Nichrome cermet fuel was recently discussed.[6] Chamberlain has more recently reported on the pilot-plant development of a continuous process of this nature,[7] as carried out at the Idaho Chemical Processing Plant (ICPP). The fuel considered is that used in the ANP Heat-Transfer Reactor Experiment (HTRE). The process involves continuous dissolution, continuous removal of chloride from the dissolver product by distillation to permit subsequent processing in stainless-steel equipment, and extraction in pulse columns. A process flow sheet resulting from the pilot-plant work, which involves process streams containing less than 10 g of uranium per liter (for criticality safety), is contained in the reference report. All steps of the process were tested with unirradiated materials and demonstrated to be workable. A process involving total consumption of the acid feed for simplicity in dissolver control is also proposed. This yields a dissolver product of one-third the volume, which, however, is diluted to the same concentration for extraction. Transfer-unit heights for chloride stripping and solvent extraction, and stage requirements, were also determined. A small residue of solids, of the order of 1 wt.% of the fuel, results from the dissolution step. This is in part chromium and silicon oxides, and in part niobium oxide. One percent niobium is used as an alloying agent in the Nichrome used in the fuel matrix.

Effects of Minor Alloy Elements on Aluminum-Uranium Alloy Dissolution

In connection with studies of causes of variability in the rate of mercury-catalyzed aluminum-uranium alloy dissolution in nitric acid, work at the ICPP[8] has indicated that a number of minor alloy elements in aluminum have a significant effect. The batch dissolution time in 6*M* nitric acid containing 0.005*M* mercuric nitrate was increased at threshold concentrations of other elements in aluminum as follows: silicon, 0.25%; copper, 0.1%; nickel, 0.2%; and chromium, 0.1%. Iron at similar concentrations accelerated dissolution; manganese and magnesium had no significant effect.

Dissolution of Beryllium and Beryllium-Uranium Alloys

Recent expansion of beryllium resources and improvements in recovery techniques, together with development of technology for space applications, indicate that this metal may find increasing application in the nuclear field. Whitfield of the Australian AEC Establishment has reported on preliminary work in dissolving beryllium in ammonium fluoride solutions.[9] In refluxing solutions a first-order type of dependence on free-fluoride concentration was observed. The solubility of tetravalent uranium was similarly proportional to the free-fluoride concentration. Consequently it appeared unlikely that ammonium fluoride would be a satisfactory solvent for beryllium-uranium alloys or mixtures where the uranium-to-beryllium ratio is small. It appeared, however, that ammonium fluoride could be used successfully as a decladding agent for an oxide fuel clad in beryllium metal.

Treatment of Nonmetallic Fuels

At Oak Ridge, studies of the composition of gases resulting from the hydrolysis of carbides have been extended to the sesquicarbide and dicarbide of uranium and to thorium carbide.[2,10] Water or dilute sulfuric or hydrochloric acid

treatment of uranium sesquicarbide resulted in half of the carbon appearing in the gas, mostly as ethane or higher hydrocarbons, and the release of much hydrogen. Water or sulfuric acid hydrolysis of a dicarbide (overall carbon-to-uranium ratio of 1.97, with some free carbon) yielded a similar gas with some methane. The gas composition accounted for only about one-third of the carbon in the carbide. Hydrochloric acid treatment yielded a gas containing more hydrogen and a lower fraction of the initial carbon in the gas phase.

Los Alamos workers have noted[11] that a mixed uranium-plutonium carbide (composition corresponding to the empirical formula $U_{0.8}$ $Pu_{0.2}$ $C_{0.95}$) can be dissolved completely in hot concentrated nitric acid containing 0.05*M* hydrofluoric acid. Uranium and plutonium can be extracted with diluted tributyl phosphate (TBP) and partitioned as in the Purex process.

Studies have been made of the processing of graphite-matrix fuels by combustion and acid leaching of the residue. If the fuel is incorporated in the graphite as pyrolytic-carbon-coated particles (of uranium-thorium carbide, for example), Ferris[12] has observed that combustion of the particle is greatly slowed and incomplete, and the recovery of the fuel from the residue is made more difficult. By soaking the fuel in lead acetate, potassium permanganate, or copper nitrate, combustion of the pyrolytic carbon is catalyzed and the ignition point is markedly lowered (from over 700°C to 300–500°C).

Separations Processes

The development of solvent-extraction technology continues to be of prime importance. Work is also being done on ion-exchange processes.

Solvent-Extraction Processes

Extraction - Process Development. Process problems concerned with Purex type processes continue to receive attention by English workers. Because a gap existed in available data for uranium distribution coefficients between low-acidity nitric acid solutions and 20% TBP in a kerosene type diluent, Holmes and others[13] have published data for this system at low uranium concentrations (0.001 to 1 mg/liter) for aqueous nitric acid concentrations between 0.0002*N* and 0.5*N*. Distribution coefficients were in the range of 0.06 to 0.07 for acidities up to 0.05*N*. Greenfield and Hardy[14] have extended data for the distribution of nitrosyl ruthenium nitrate complexes between strong nitric acid and undiluted TBP. As predicted, the distribution coefficient for the ruthenium complexes decreased as the acidity was increased above about 1*M* until a minimum was reached at about 12*M* nitric acid. Coefficients varied with time and did not reach an equilibrium level for many hours. Studies of using a tetravalent uranium compound for plutonium partition in the Purex process have also been made by British workers. Electrolytic reduction of uranyl nitrate to the tetravalent uranium state is favored. Since the solution slowly reoxidizes, a nitrite-destroying stabilizer is desired. Sulfamic acid, urea, and hydrazine are among materials that may be used for this purpose. Streeton and Jenkins[15] note that urea is relatively ineffective as compared to sulfamic acid and hydrazine. Sulfamic acid is disadvantageous inasmuch as it introduces the undesirable sulfate ion into the plant wastes. Thus it appears that hydrazine is to be preferred as the stabilizing material.

In this country[16] both Savannah River and Hanford have been doing extensive investigations on the use of U(IV) as a reducing agent for plutonium partition. If successful, this method will decrease the volume of radioactive waste going to tank storage.

Siekierski of the Polish Academy of Sciences has made an extensive study of the effect of the nature of the diluent used with TBP on distribution coefficients for thorium and europium from a sodium nitrate-salted aqueous system.[17] A group of 14 diluents was used, ranging from kerosene and heptane through benzene and toluene to various halogenated hydrocarbons. The TBP concentration was held at 5 vol.%. Organic-to-aqueous distribution coefficients with bromoform and chloroform as diluents were very low, but otherwise the values with a given aqueous phase fell within about an order of magnitude. The highest distribution coefficients were obtained for aliphatic diluents with somewhat lower values being obtained with aromatic and substituted aromatic diluents. An explanation is attempted on the basis of the activities of the complex agent and the complex formed.

Alternate Solvent Systems. A novel extraction process has been prepared by Charles F. Coleman at Oak Ridge as an alternate to TBP extraction for the recovery of uranium from zirconium-uranium alloy fuels after dissolving in hydrofluoric acid and hydrogen peroxide. This is called the Neuflex process since it uses a neutral rather than an acidic feed to solvent extraction and extraction is accomplished from a fluoride rather than a nitrate system. This requires that a more strongly complexing solvent be used, and di-2-ethylhexyl phosphoric acid (D2EHPA) in combination with trioctylphosphine oxide or diamylamyl phosphonate in a hydrocarbon diluent is proposed. Uranium is recovered by stripping with ammonium carbonate solution. A tentative dissolution-extraction flow sheet, as recently proposed,[18] is shown in Fig. II-1.

In another application of amines as extractants in separations processes, David J. Crouse at Oak Ridge has found that tertiary amines can be used to extract sulfuric acid from solutions used to dissolve stainless-steel cladding, e.g., from uranium dioxide fuels, to permit recycle of the acid. This reduces the volume of waste from such a process and might offer economies in respect to acid consumption. Tertiary amines of fairly high molecular weight appear to be favored for this application. With

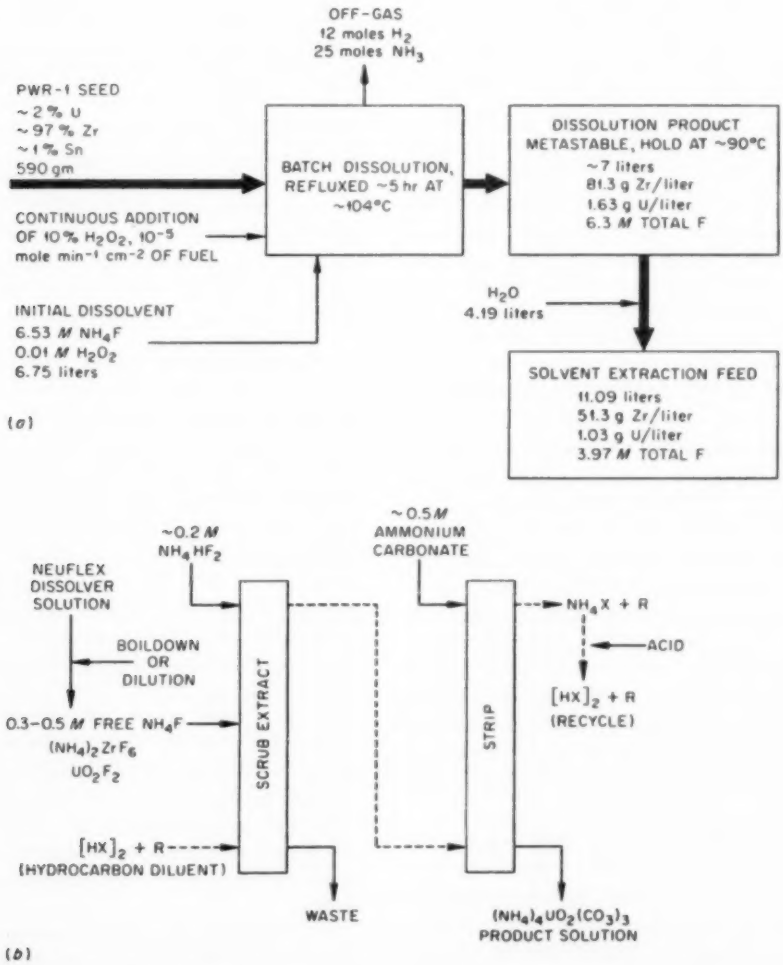

Fig. II-1 Neutral fluoride extraction process for zirconium alloy fuel.[18]

a 0.2*M* solution of *N*-benzyl-di(2-ethylhexyl)-amine in a kerosene type diluent (Amsco 125-82), containing 16% isodecanol, it appeared possible to recover over 90% of the sulfuric acid from a solution containing 2.5*M* sulfuric acid and 1.0*M* ferrous sulfate. The acid was readily stripped from the organic phase with water to yield about a 1*M* solution that would only require concentration for recycle. Iron, chromium, and nickel are not extracted under these conditions. The behavior of uranium lost to the decladding solution was not reported.

Solvent Stability and Treatment. The performance of TBP type solvents in separating uranium and plutonium from fission-product contaminants is frequently limited by the presence of impurities or degradation products introduced with or derived from either the solvent or the diluent. Under certain conditions extraction of some part of the Zr^{95} initially present, or of its niobium daughter, may contaminate the product streams or interfere with cleanup of the recycle solvent stream.

Rainey and Moore[19] of the Oak Ridge National Laboratory (ORNL) have recently reported on the extractability of niobium at tracer levels from nitric acid solutions by fresh and degraded TBP-diluent systems. The variation of distribution coefficients on successive contacts was used to determine fractional extractability, which is the result of varying proportions of several chemically different species of niobium present. Less than 30% of the niobium present was extractable by a mixture of 30% freshly purified TBP in dodecane from solutions 0.1*N* to 4.0*N* in nitric acid; the amount decreased to less than 5% as the acidity decreased. The distribution coefficient of the extractable portions also varied from 0.008 to 0.05, indicating the transfer of more than one species. If one-tenth of the TBP had been recently degraded by boiling with nitric acid, more than 80% of the niobium became extractable, and if the diluent included an Amsco hydrocarbon fraction that had also been degraded, niobium extractability exceeded 95%.

Effects of solvent impurities have been noted in Purex-plant performance at Hanford. Recently the use of an alkaline permanganate solution was adopted for treatment of second-cycle Purex solvent.[20] Performance of the 2D and 2E uranium-purification columns was markedly improved. The reason for the original deterioration in solvent quality has not been specifically established.

At Oak Ridge an extensive study of liquid reagents for the removal of deterioration products from used solvent has been carried out.[21] Scrubbing tests were conducted with nearly 100 liquids or liquid-solid combinations. The most effective cleanup was achieved by treatment with enthanolamines, thereby confirming results of British work.[22] The reagents were evaluated by scrubbing a degraded TBP-diluent mixture, contacting the latter with solid calcium hydroxide, and then determining the ability of the solvent to extract zirconium-niobium tracer from 2*M* nitric acid. Scrubbing four times with ethanolamine substantially restored to degraded solvent the low extractability of the fresh material.

Use of ethanolamine for this purpose is accompanied by some disadvantages. It may not be economical if needed on about an equal-volume basis, unless a low-cost means for regenerating ethanolamine is developed, since the cost of the ethanolamine is about the same as that of fresh TBP-diluent mixture. Further, there is some mutual solubility of the scrubbing reagent in the solvent and of TBP in the ethanolamine. The effect of a small amount of ethanolamine on the decontaminating effectiveness of the TBP solvent was not reported.

Separation of Transuranium Elements. Coleman at Oak Ridge has reported[23] further tests of the previously described[6] amine extraction process for final purification of plutonium separated by the Purex process. Flow-sheet changes included an increase in the solvent-feed ratio (with a lower amine concentration), high-acid scrub (5*N* or 6*N* nitric acid compared with 0.5*N* in earlier tests), and variations in the acetic acid concentration of the strip solution. Excessive plutonium refluxing in the strip section suggested that a high-acid scrub should be followed by one of low acidity to decrease acid carryover from extraction to strip sections. In hot-cell tests with an actual first-cycle plutonium product solution, gamma decontamination factors of only 100 to 500 were observed, as compared with values of the order of 50,000 in zirconium tracer tests. Inferior performance may be attributable to aging of the feed.

Other Recovery Processes

Further work is reported from Oak Ridge[2,3] on the tertiary amine and phosphonate processes

for recovering, decontaminating, and separating transuranium elements up to californium from lithium chloride solutions of products of plutonium and higher element irradiation. The Alamine extraction process previously described[6] was tested for ruthenium and zirconium removal. Zirconium and ruthenium were quantitatively extracted (the latter only when an oxidant like peroxide was present), and in the stripping operation, both showed distribution coefficients highly in favor of the solvent when about 9*M* hydrochloric acid was used. A report on the development of the phosphonate transuranic partition flow sheet has been given by Baybarz.[24]

Ion-Exchange Processes

Watson has recently published[25] the results of an extensive and careful study on the kinetics and mechanism for the exchange of uranyl sulfate with the strong base anion resin Dowex 21K. This summarizes work undertaken at Oak Ridge some years ago.[26]

A mathematical model was developed for the absorption and elution of uranium as an anionic complex, considering various possible forms of the complex and of other ions in sulfate and chloride (or nitrate) systems. The problem was simplified by assuming that all the uranium was present as a single complex ion and that only the movement of this complex, and of the sulfate or chloride ions, is needed to describe the process. Exchange ratio and self-diffusion rates were measured using radioisotope techniques for uranium, sulfate, and chloride (no convenient radioisotope was available for measuring nitrate exchange). Many of the data were obtained by rate measurements with single beads, but a technique permitting larger samples and using a submerged pump contactor was employed for more precise work.

This study indicated that, over a wide range of solution concentrations, uranyl sulfate loading rates were governed by a single type of uranium ion, having a charge of −2, counter-diffusing with sulfate or chloride ions. The ion within the resin is probably $UO_2(SO_4)_2^{2-}$. The rates at which uranyl sulfate can be eluted from an anion resin by sodium chloride solution also appeared to be governed by a single type of uranium ion, but one which is of different nature than that involved in sulfate loading. It was not possible to measure the charge of this ion, but it is probably UO_2^{2+}.

"Gel-Liquid Extraction"

Mall has recently suggested an ion exchange-like separations technique, using resin beads to absorb a liquid extractant, which he calls gel-liquid extraction.[27] The application of this technique to the separation of europium and americium was investigated briefly at Oak Ridge.[23] Beads of styrene-divinyl benzene copolymer, swollen with Alamine 336 in di-isopropylbenzene to contain about 7% amine, were placed in a 43-cm glass column. The americium and europium tracers were adsorbed onto the beads from very slightly acid 13*M* lithium chloride solution. Europium was then eluted by a similar lithium chloride solution at flow rates of 0.3 to 1.1 ml/(cm^2)(min), and americium by less concentrated lithium chloride (9*M* or 11*M*). Sharp and quantitative separations were obtained. However, since flow rates and the extractant concentration in the resin are low and some difficulties were encountered in packing due to bead sticking, and since liquid-liquid extraction can provide a separation factor of 100 for the system, further work on this process for transuranic separations did not appear to be warranted.

Process Instrumentation

Butler reports[28] on a simple flow monitor for radioactive corrosive liquids that has been in service for 18 months at Savannah River. The instrument uses conductive probes wired into a suitable electrical warning circuit. Figure II-2 shows a cutaway view of the flow chamber, and Fig. II-3 shows the electrical schematic. This monitor was designed and constructed to survey the flow of a caustic solution used to absorb radioactive contaminants but, of course, could be used on any conducting solution. Alarm is given when the flow decreases as well as when plugging of the waste line occurs.

As can be seen in Fig. II-2, the flow-monitoring section consists of a pencil-point probe located near the spill end of a horizontal V-shaped trough long enough to damp out turbulence. The setting of the probe above the vertex of the trough is adjustable and thus permits volumetric calibration and surveillance of the flow.

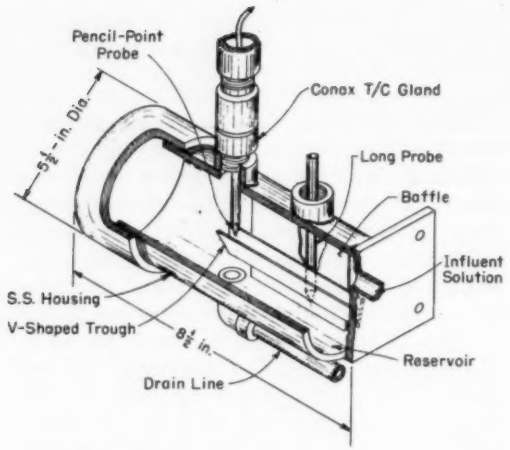

Fig. II-2 Cutaway view of liquid-flow monitor chamber.[28]

The bottom of the chamber serves as a reservoir in case the drain line becomes plugged. The long probe is used to detect the solution level in the reservoir and is set at a height to give suitable time for adjustments after annunciation.

This particular monitor was made from stainless steel and calibrated for a flow of 300 cm^3/min but, of course, could be adapted for larger scale operation and could be constructed from other materials.

Plant and Equipment Design and Operation

Shearing Device

Abbatiello[29] describes a shear adaptable for remote use in removing contaminated process equipment. The shear, shown in Fig. II-4 (model MC-125-DA made by Manoc Manufacturing Company), has 7-in.-wide cutting blades capable of opening 5 in. Rotation is possible about its axis for a total of 280°, and the unit can be mounted by use of a bolting circle at the top. Detachable hoses connect the shear with the hydraulic power unit. A maximum pressure of 8800 psi makes it possible to shear up to 4-in. schedule-40 stainless-steel pipe.

The report further describes possible ways of using the shear; however, it would, of course, operate best if the cell were designed for its use from the start. A crane or some means of locating the shear inside the cell must be provided. Viewing could be difficult unless the cell had windows or a very good television system. It was reported that a closeup-view television camera and an overall-view television camera worked fairly well.

Solvent-Extraction Contactors

One of the limiting factors in solvent extraction is solvent damage by radiation, par-

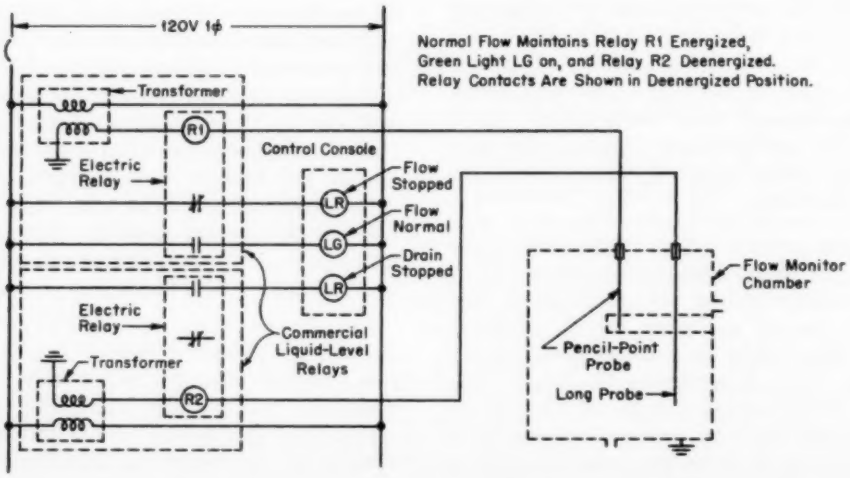

Fig. II-3 Electrical schematic diagram for liquid-flow monitor.[28]

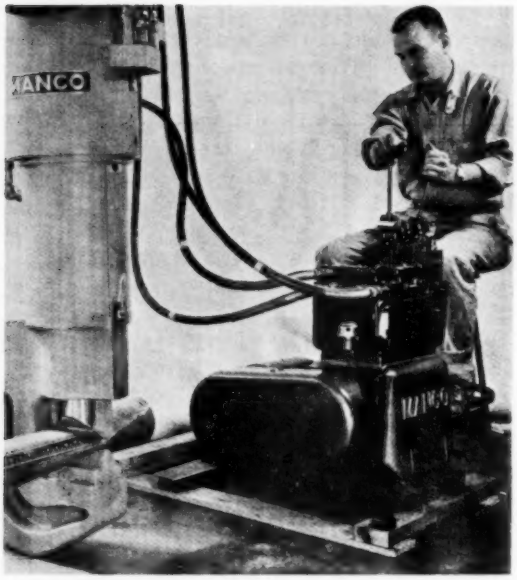

Fig. II-4 Hydraulic shear cutting a 4-in. schedule-40 stainless-steel pipe.[29]

ticularly with the higher burnup of fuel and the desire for shorter cooling time. Both Oak Ridge and Savannah River have undertaken to solve this problem by developing extraction equipment allowing short contact time.

ORNL reports on their work[18,30] with stacked clone contactors, a countercurrent pump-driven staged device consisting of hydroclones aligned axially with the overflow of a given stage and the underflow of the adjacent stage entering a concentric chamber from which the stage recycle pump takes suction. Figure II-5 shows a closeup view of several stages made from transparent plastic material.

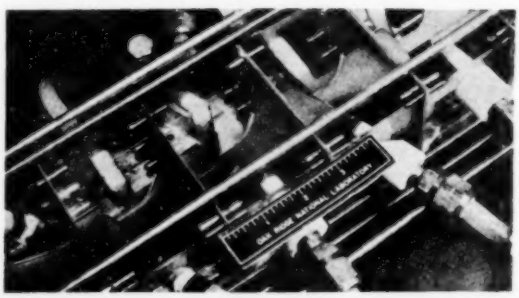

Fig. II-5 ORNL stacked clone contactor.[18]

In general, $1\frac{1}{2}$-in.-diameter spin sections and $\frac{1}{2}$-in.-diameter cylinders with various transition section and underflow geometries were used. For most runs, seven stages were mounted on the rack, each stage being driven by a small centrifugal pump. The organic feed was introduced into the discharge line of the appropriate stage pump using a centrifugal feed pump. The clone stages below this point then served as polishers to return entrained organic. Aqueous feed entered the cascade in the suction line of the first-stage recycle pump from an elevated tank. Raffinate left the cascade under a hand-fixed restriction. A rotameter aided in keeping the rate constant, but absolute rate was measured by a calibrated tank. Organic product left

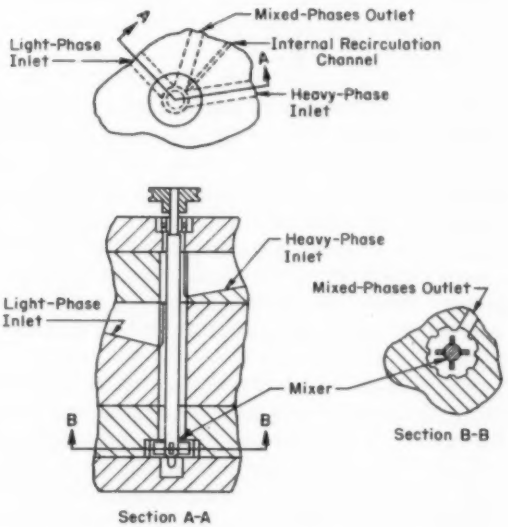

Fig. II-6 Mixer and mixing chamber of miniature centrifugal contactor.[31]

the cascade by simple overflow. Suitable flow and temperature controls were provided.

Many data are presented in tables for a series of evaluation runs, using various stage arrangements (feed rates, etc.) for the system: 1 *M* sodium nitrate, 18.3% TBP-Amsco.

Stage efficiencies were reported at 2 to 76% with the best arrangements giving 40 to 75%. Organic retention times of less than 30 sec per theoretical stage were reported.

Jennings at Savannah River reports[31] on a similar study using a miniature centrifugal contactor. Figures II-6 and II-7 show sections

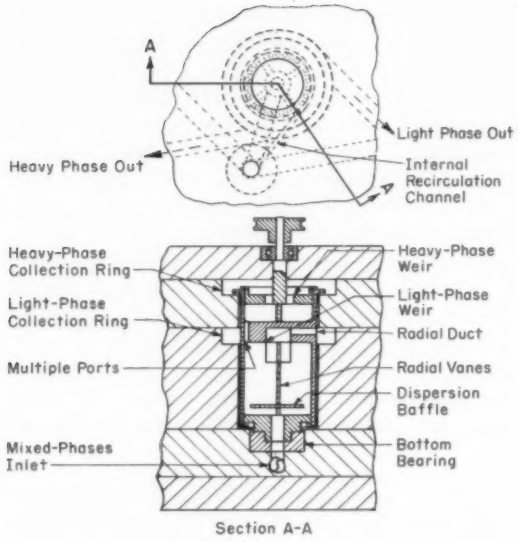

Fig. II-7 Centrifuge bowl and housing of miniature centrifugal contactor.[31]

of the mixer and centrifugal bowl. Figure II-8 shows a top view of a four-stage unit with a Plexiglas housing to permit observation. The mixer paddle is $\frac{1}{2}$ in. in diameter by $\frac{3}{16}$ in. in height. Figure II-9 shows an exploded view of a centrifugal bowl approximately $\frac{3}{4}$ in. in diameter.

The radial vanes, shown in Fig. II-9, keep liquid rotating at the same speed as the bowl for the most effective settling. Since efficient operation requires that the spacing of the two discharge weirs match the densities of the liquids, a derivation is presented showing that this design should separate liquid pairs with density ratios of 0.66 to 0.90 with a residence time of 6 sec per stage.

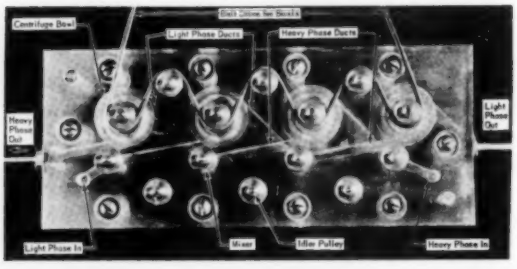

Fig. II-8 Top view of assembled centrifugal contactor.[31]

Several runs were made with suitable feed controls, mechanical drives, etc., for residence times of 3 to 6 sec per stage with aqueous flow rates up to 300 cm^3/min (higher rates caused liquid to back up from the mixer to the flow channels, thereby flooding the unit).

Data were presented showing mass-transfer efficiencies of 95% for uranium transfer in both nitric acid–TBP and aluminum nitrate–TBP systems. Good results were obtained at mixer speeds of 5000 rpm and bowl speeds of 4000 to 7000 rpm.

Several tables and curves are given which present the data very clearly.

Also given is the design of a 16-stage "mini" centrifugal contactor. The housing for this is stainless steel, and the stages are arranged in a circular configuration that allows a central gear to drive all bowls and a gear train to drive all mixers.

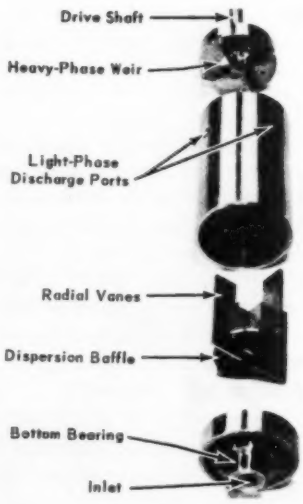

Fig. II-9 Exploded view of centrifuge bowl.[31]

Aqueous Homogeneous Reactor Fuel Processing

ORNL, at the request of AEC's Division of Reactor Development, has made conceptual plant studies for on-site fuel processing and fuel reconstitution facilities for the AHBR (Aqueous Homogeneous Breeder Reactor). The studies were based on a thorium-U^{233} fuel cycle used

with a heavy-water moderator. Conceptual design and cost estimates were made for a reactor of 1000 Mw(e) power output.[18]

The fuel-processing flow sheet used is based on the daily removal and processing of a fraction of the uranyl sulfate–heavy water core solution and the thoria blanket pellets. The core solution is continuously run through a hydroclone in the reactor fuel circuit to remove solids. A small part of the overflow is continuously bled off, evaporated to 75 g of uranium per liter, and allowed to decay for seven days. The uranium is precipitated as UO_4, which is filtered; the precipitate is redissolved in D_2SO_4 and returned to the core. The filtrate is evaporated for D_2O recovery and then diluted to 4*M* sulfate. The slurry underflow from the hydroclone is also evaporated for D_2O recovery. The resulting solids are dissolved in 10.8*M* H_2SO_4 and then combined with the filtrate from the UO_4 filtration; this is stored for a 90-day decay period before solvent extraction.

The thoria pellets from the blanket are dissolved in 13*M* HNO_3–0.04*M* HF–0.1*M* $Al(NO_3)_3$. This solution, the 90-day-decayed dissolved hydroclone bottoms, and the UO_4 filtrate are combined and solvent extracted to effect thorium-uranium-protactinium separation. The recovered thorium nitrate is converted to thoria, pelleted, and returned to the reactor. The uranium nitrate is converted to uranyl sulfate in D_2O by UO_4 precipitation and the subsequent dissolution of the cake in D_2SO_4. The fuel is then returned to the reactor core.

For the design and cost studies, two reactor concepts were considered. In one case, in which the reactor has a core-to-blanket thermal-power ratio of 60:40, the processing-plant blanket capacity required is 266 kg of throium per day containing 2.84 kg of uranium. In the alternative case, in which the core-to-blanket thermal-power ratio is 90:10, the required daily processing capacity is 1117 kg of thoria containing 3.0 kg of uranium.

The smaller processing plant for the first case would require a canyon 257 ft long by 29 ft wide containing six processing cells, three maintenance service cells, and a crane maintenance area. The larger plant for the second case is similar to the smaller except that the canyon area is 277 ft long by 31 ft wide, and the maximum shielding is 7 ft compared to 6.5 ft for the smaller plant. The total capital investments for the two conceptual plants were calculated to be $13.9 and $15.7 million, respectively.

Corrosion and Construction Materials

The Chemical Technology Division of ORNL has published its annual report[18] for the period ending June 30, 1962. The report summarizes the corrosion work that was performed during the period and the process background that existed. Many of the data presented were included earlier in routine monthly and quarterly progress reports and were reviewed in *Reactor Fuel Processing* when those reports were published. Corrosion work related to the following processes was reported: (1) the combination of Darex and Zirflex processes, (2) the modified Zirflex process, (3) clarification of dissolver solutions from the Darex, Sulfex, and Zirflex processes by means of a multipurpose centrifuge, (4) the fused-salt volatility process, and (5) waste calcination process. Information not previously reviewed in *Reactor Fuel Processing* is included below.

Corrosion tests of stainless-steel specimens have been performed under conditions being investigated for purifying of plutonium from Purex-process product streams. One of the methods utilizes an extraction technique with trilaurylamine in diethylbenzene as the solvent. Contemplated strip solutions are 2*M*, 3*M*, or 4*M* acetic acid diluted with nitric acid that is introduced as a scrub solution. Type 347 stainless steel was tested in a refluxing environment of the nitric-acetic acid mixtures used for the stripping. The maximum rate of attack observed was 0.02 mil/month, based on a 96-hr exposure in 1*M* nitric acid–2*M* acetic acid–45 g of uranyl nitrate hexahydrate per liter. The specimen was exposed as a steam tube through which heat was supplied to the solution at a heat flux[18] of about 5000 Btu/(hr)(sq ft).

Use of mixtures of nitric and hydrofluoric acids for the dissolution of some power-reactor fuels has been considered in the past. However, for this environment the construction materials problems have been particularly severe. Corronel 230, an alloy developed by a British firm (Henry Wiggins, Ltd.) presumably for the specific purpose of resisting this kind of acid mixture, has the nominal composition 65%

nickel and 35% chromium. Although Oak Ridge is not presently considering a power-reactor processing scheme involving these acid mixtures, corrosion evaluations and comparisons have been made of this alloy and of other construction materials contemplated for use with the Darex, Zirflex, and Sulfex processes (Table II-1).[18] The superiority of Corronel 230 to low-carbon Hastelloy F, stainless-steel type 309SCb, and two experimental Haynes alloys in boiling 10*M* nitric acid–0.5*M* hydrofluoric acid is clear. However, a corrosion rate of 60 mils/month is probably not acceptable for service. With decreasing nitric and increasing hydrofluoric acid contents, the corrosion rate further increases.[18]

Construction materials for the Darex, Zirflex, and Sulfex decladding procedures have been established in recent years by work at Hanford, Idaho, and Oak Ridge. Less attention has been devoted to whether optimum materials for those decladding processes are compatible with the subsequent uranium dioxide dissolution process. In studying this, Oak Ridge has exposed alloys such as Nionel, low-carbon Nionel, Hastelloy F, and Nichrome V to various solutions typical of those used in uranium dioxide dissolution. Although no conclusions were given in the annual report, the results that were presented are tabulated in Table II-2.

At ORNL, plans are progressing for the isolation and recovery of transuranium elements.[32] Processes presently envisioned make use of concentrated chloride solutions covering a wide range of acidities. In some process steps, nitrate will also be present. In all solutions containing an appreciable concentration of the transuranium elements, peroxide is expected to be present as a product of the radiolysis of water.

In an exploratory corrosion test program to select construction materials for these processes, specimens of 25 metals and alloys were exposed in the liquid, vapor, and interface regions of a number of simulated process solutions. The results of tests in which the six best alloys were exposed to possible synthetic processing environments are shown in Table II-3. Attack on weld specimens in all environments was uniform. In recent more intensive tests in chloride-containing solutions, corrosion rates of Hastelloy B were in reasonable agreement with those shown in the table. Hastelloy B has been eliminated from consideration as a construction material for the transuranium processing facility.

Hastelloy C was subjected to varying degrees of preferential attack in heat-affected zones, and this undoubtedly was responsible for the increased corrosion rates with increased exposure time. This attack was eliminated by the use of a postweld heat-treatment at 2250°F, but the overall corrosion resistance was not improved. Corrosion resistance of Hastelloy C was extremely poor in all chloride-containing solutions at elevated temperatures.

Niobium was reasonably resistant to all oxygenated environments tested. There was evi-

Table II-1 CORROSION OF VARIOUS ALLOYS IN MIXTURES OF NITRIC ACIDS AND HYDROFLUORIC ACIDS[18]

Metal	Solution	Temp., °C	Exposure time, hr	Corrosion rate, mils/month
Corronel 230, unwelded	10*M* HNO_3–0.5*M* HF	116	96	60
Corronel 230, unwelded	10*M* HNO_3–0.5*M* HF	60	96	3
Low-carbon Hastelloy F	10*M* HNO_3–0.5*M* HF	116	96	>200*
S.S. 309SCb	10*M* HNO_3–0.5*M* HF	116	96	>200*
Haynes EB4358†	10*M* HNO_3–0.5*M* HF	116	96	>200*
Haynes EB5459†	10*M* HNO_3–0.5*M* HF	116	96	>200*
Corronel 230	10*M* HNO_3–0.5*M* HF–0.75*M* $Al(NO_3)_3$	116	408	0.7
Titanium	10*M* HNO_3–0.5*M* HF–0.75*M* $Al(NO_3)_3$	116	408	0.3
Corronel 230	1*M* HNO_3–3*M* HF	116	4	>2700
Corronel 230	1*M* HNO_3–3*M* HF	60	4	5
Corronel 230	1*M* HF	Boiling	2	44
Corronel 230	1*M* HF–0.06*M* H_2O_2	Boiling	?	13

*Aggressive localized attack.
†Experimental alloys.

Table II-2 CORROSION OF VARIOUS ALLOYS IN NITRIC ACID BASED SOLUTIONS[18]

(Temperature: Refluxing)

Metal	Location	HNO_3 concentration, *M*	Time, hr	Corrosion rate, mils/month	Comments
Nichrome V	Vapor	4	672	0.2	Incipient grain-boundary attack
INOR-8	Liquid	4	115	>290	Specimen disintegrated
Nionel	Vapor	4	300	1.3*	Agressive intergranular attack
Nionel	Vapor	6	648	1.9*	Agressive intergranular attack
LCNA	Vapor	6	672	1.9	Intergranular attack
Hastelloy F	Vapor	6	672	2.3	Intergranular attack
Nionel	Vapor	10	648	7.2*	Agressive intergranular attack
Nionel	Vapor	12	648	20.0*	Agressive intergranular attack
Nionel	Vapor	15.8	648	36.0*	Agressive intergranular attack
Corronel 230	Liquid	20 to 23	384	7	Intergranular attack
Titanium	Liquid	20 to 23	384	0.07	
Titanium	Liquid	20†	164	0.03	
Mild steel	Liquid	20†	164	688	
Type 1100 aluminum	Liquid	20†	164	127	
Type 6061 aluminum	Liquid	23‡	144	0.01	
S.S. type 304SCb	Liquid	23‡	144	0.6	

*Corrosion rate increased with time.
†Additives: 50 g of graphite and free graphite per liter.
‡Additive: 0.1*M* HF.

Table II-3 CORROSION OF ALLOYS IN TRANSURANIUM PROCESSING SOLUTIONS[32]

(Numbers in Parentheses Are Hours of Exposure)

Solution	Corrosion rate, mils/month					
	Hastelloy B	Hastelloy C	Niobium	Tantalum	Titanium	Zircaloy-2
Temperature: 43°C						
3*M* HCl–O_2	3	13 (336)*				<0.1 (336)
6*M* HCl–O_2	6	6.6 (200)*				
6*M* HCl–H_2O_2	12	14 (200)				
8*M* HNO_3–O_2		3 (1008)				Nil
3*M* HCl–1*M* HNO_3–O_2		1 (336)				
Temperature: 105 to 128°C						
6*M* HCl (no O_2)				Nil (168)	>100 (3)	0.1 (96)
6*M* HCl–O_2			0.6 (900)			<0.1 (336)
6*M* HCl–H_2O_2		125 (24)			>500 (24)†	1 (96)
6*M* HCl–8*M* HNO_3 (no O_2)				Nil (168)	0.3 (72)	14 (24)
10*M* LiCl–0.1*M* HCl–O_2	3 (168)			Nil (24)	>900 (3)	
10*M* LiCl–0.1*M* HCl–H_2O_2	2 (?) 44 (48)			Nil (120)	<0.1 (120)‡	
10*M* LiCl–0.5*M* HCl–O_2			0.3 (900)			

*Preferential attack in heat-affected zones; increasing rate with time; preferential attack eliminated by heat-treatment.
†Titanium–0.1% palladium.
‡Temperature: 85°C

dence that the presence of hydrogen peroxide and/or lanthanum chloride accelerates the rate of attack, but additional testing will be required to resolve this. In tests in which niobium was coupled with two pieces of aluminum when exposed to hot 6*M* hydrochloric acid solution, the aluminum dissolved rapidly and copious quantities of hydrogen gas were evolved. After seven such exposures, the niobium fractured due to hydrogen pickup during the test. A hydrogen content of 960 ppm was measured following a test in which the niobium was coupled to aluminum, as compared with 4 ppm when the niobium was exposed without aluminum.

Tantalum was found to be chemically inert in the chloride-containing solutions at all temperatures. Some evidence of hydrogen pickup was obtained in a dissolving test similar to the one described for niobium. Following seven exposures in which the specimen was coupled with two pieces of aluminum, it was found to contain 54 ppm hydrogen. The hydrogen content of an unexposed control specimen was 1 ppm. No cracking of the exposed specimen was observed during a 180° bend test.

The corrosion behavior of titanium was affected by the presence of an oxidizing species in the chloride-containing solutions. When sufficient quantities of hydrogen peroxide or nitric acid were present, resistance to corrosion was acceptable. In the absence of such an oxidant, corrosion was generally catastrophic. Titanium was eliminated from consideration as a construction material for the transuranium processing facility.

Zircaloy-2 showed excellent resistance in flow tests with high-temperature 6*M* hydrochloric acid whether or not hydrogen peroxide was present. Corrosion was severe in the

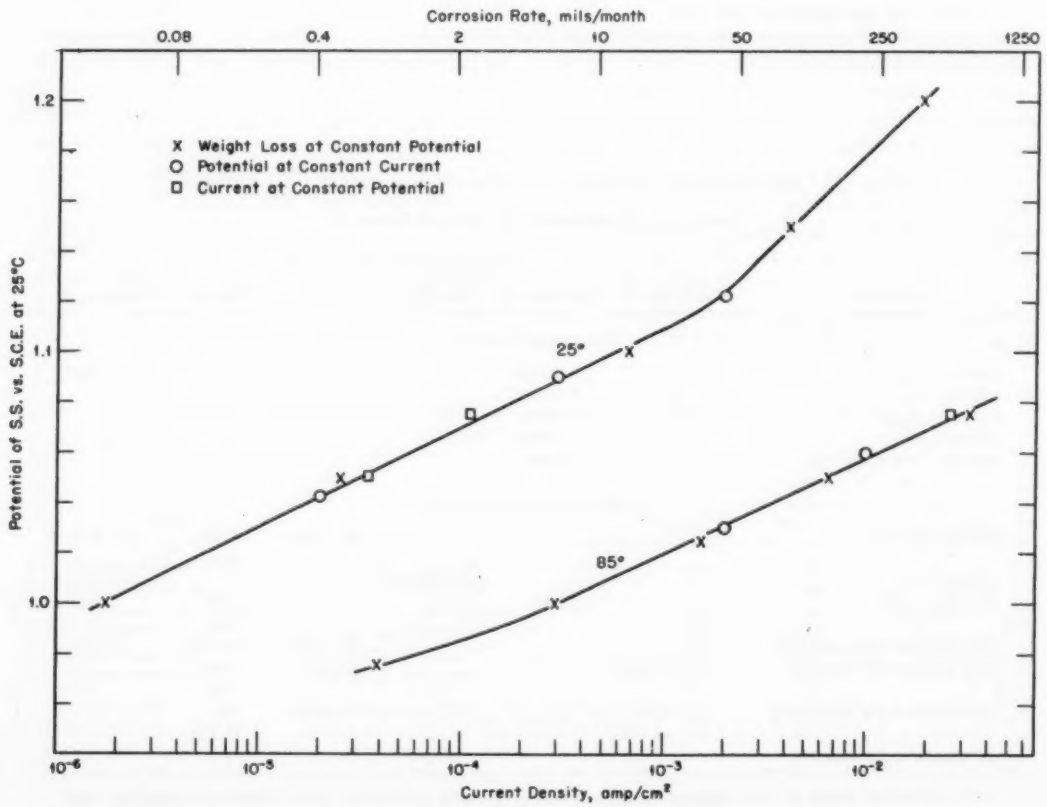

Fig. II-10 Potential-current density (corrosion rate) relations for type 304 stainless steel at 25 and 85°C in a dissolver solution containing 5*M* nitric acid.[35]

mixed hydrochloric–nitric acid system at 105°C.

Idaho Processes

A topical report on the sodium fluozirconate precipitation process for zirconium fuels has been published by ICPP.[33] Corrosion information relating to the precipitation portion of the process has been covered previously in *Reactor Fuel Processing*.[34] The corrosion resistance of stainless-steel type 316L, Hastelloy F, and Carpenter-20 was determined for the step in which the filtrate from the precipitation process, together with precipitate wash solutions, is boiled down for further zirconium and fluoride removals prior to the uranium solvent-extraction step. The maximum corrosion rate observed for any of the alloys was 4.2 mils/month.

The ICPP is investigating the possibility of converting its batch type dissolutions of zirconium fuels to continuous processing. Continuous dissolution runs are being made in the pilot plant in a ½-in.-diameter dissolver. No visible corrosion has been noted within the Monel dissolver.[35] Corrosion evaluations are being made simultaneously on coupons exposed to dissolver product resulting from the dissolution of Zircaloy-2 or uranium–Zircaloy-2 alloy in various hydrofluoric acid solutions at temperatures of 80 to 90°C. The corrosion penetration rates resulting from a total of 46 hr exposure were determined to be 5 and 0.2 mils/month, respectively, for Monel and Carpenter-20 Cb coupons exposed.

Both Savannah River and the ICPP continue to study electrolytic dissolution of power-reactor fuels. Recent studies at the ICPP[35] are reported in which corrosion rates of austenitic stainless-steel type 304 are related to the applied potential (vs. a standard calomel electrode) and temperature. Such data will be needed if cathodic protection is used for stainless-steel processing equipment containing dissolver solutions at high temperatures. Such data may also be used to monitor the instantaneous corrosion rate of specific regions in contact with electrolytic dissolver process streams. Potential-current relations were established at 25 and 85°C for a typical synthetic dissolver solution containing 1*M* nitric acid plus 4*M* nitrate ions from the ferric and nickel nitrates used. Hexavalent chromium was added in the form of chromic anhydride. This information is presented in

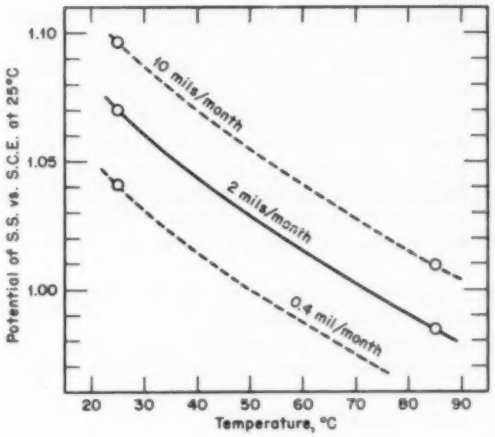

Fig. II-11 Corrosion rates as functions of potential and temperature for type 304 stainless steel in a dissolver solution containing 5*M* nitric acid.[35]

Fig. II-10. If one assumes a constant heat of activation ($\Delta H\ddagger$) over this temperature range (and this assumption is to be checked in future experiments), the data from Fig. II-10 can be used in conjunction with the relation

$$\left[\frac{\partial \ln I}{\partial(1/T)}\right]_E = -\frac{\Delta H\ddagger}{R}$$

to determine corrosion rate as a function of potential and temperature, as has been done in Fig. II-11. It is recognized that these data are valid only for the specific dissolver solutions studied and that some variations might be expected with a change in the assumed dissolver-solution composition.[35]

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Section

III

Reactor Fuel Processing

Research and Development on Nonaqueous Processing

Volatility Processes

Fused-Salt Volatility Processes

Application to Zirconium-Containing Fuels. In the fused-salt fluoride-volatility process being developed at ORNL, zirconium-uranium alloy fuel is dissolved in molten fluoride by sparging with hydrogen fluoride, and then uranium hexafluoride is produced by fluorine sparging in a separate vessel. Fourteen runs were made in the ORNL Volatility Pilot Plant to demonstrate flow-sheet operation in the processing of uranium-zirconium alloy fuel.[1] In the flow sheet used, the fuel elements were dissolved in equimolar molten sodium fluoride–lithium fluoride containing 24 to 45 mole % zirconium tetrafluoride at 650 to 500°C, by means of a hydrogen fluoride sparge, which converted the zirconium-uranium alloy to zirconium tetrafluoride and uranium tetrafluoride, both soluble in the fluoride salt. The uranium tetrafluoride was converted to volatile uranium hexafluoride by fluorination at 500°C with elemental fluorine in a different vessel, and the uranium hexafluoride was further decontaminated from fission products by absorption on and desorption from a sodium fluoride pellet bed at 100 and 400°C, respectively. The product uranium hexafluoride was collected in cold traps. Three types of feed material were used: (1) nonirradiated simulated-fuel-element Zircaloy-2, (2) nonirradiated fully enriched zirconium-uranium alloy, and (3) high-burnup long-decayed zirconium-uranium alloy.

The three runs with Zircaloy-2 elements had as their major objective the evaluation of a new dissolver off-gas scrubbing system. Previous studies had shown that submicron-size solids were generated during the alloy-dissolution step carried out with the hydrogen fluoride off-gas. A schematic drawing of the modified hydrogen fluoride system containing the off-gas scrubber is shown[2] in Fig. III-1. The gas leaving the dissolver is contacted with cold, recycled liquid hydrogen fluoride in the flash cooler, and this fluid mixture flows down the long pipe of the scrubber into a disengaging section (HF catch tank). At this point the liquid hydrogen fluoride is continuously revaporized in a reboiler, leaving the solids as a sludge in the catch tank. Periodic draining of the catch tank removes the solids. Average solids removal of more than 99% was reported. This scrubbing system is regarded as a major engineering improvement in fused-salt pilot-plant operation. Dissolution rates and efficiencies for the 14 dissolution runs are given in Table III-1.

A schematic drawing of the fluorination system is shown[2] in Fig. III-2, and a diagram of the moving-bed sodium fluoride absorber is shown[2] in Fig. III-3. The absorber operates in the following manner. On the sorption cycle, gas leaving the fluorinator first passes upward through the lower, right-angled section (hot

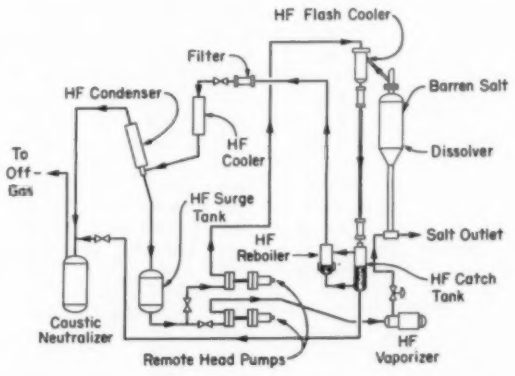

Fig. III-1 Hydrogen fluoride system of the ORNL Volatility Pilot Plant.[2]

trap) at 400°C and then flows through a temperature transition zone and into absorber No. 1 at 100°C where uranium hexafluoride is absorbed by sodium fluoride. Waste gas leaves at the midpoint of the nearly vertical section of the absorber, and a gas back-purge prevents contamination of the upper section of the absorber unit (absorber No. 2). On the desorption cycle, the temperature of absorbers 1 and 2 is raised to 400°C and the uranium hexafluoride product is swept out at the top of absorber No. 2 by a stream of fluorine introduced below absorber No. 1. A piston pushes sodium fluoride pellets from the bottom of the absorber into the dissolver at a rate determined by process requirements.

A summary of the fluorination results of the runs is given in Table III-2. Table III-3 gives the cation impurity concentrations in the product, and Table III-4 lists the fission-product decontamination factors. The higher cation impurities in run TU-10 (Table III-3) are attributed to channeling of gas through the sodium fluoride absorber.[1] The comparison of contamination levels in the product with pertinent AEC specifications is shown in Table III-5.

Application to Short-Decayed Uranium Dioxide Fuel. In laboratory tests at ORNL,[1,3] uranium recovered from irradiated uranium dioxide fuel decayed 15 to 30 days was decontaminated from short-half-life fission products by the fused salt–fluoride volatility process. Activity levels in the product are summarized in Table III-6. Radioactive iodine and tellurium, which form volatile fluorides, were effectively separated from the uranium hexafluoride product in the sodium fluoride absorption step. Radioactive niobium, ruthenium, and zirconium behaved as expected from the results of previous work, with good decontamination of the uranium hexafluoride product from their respective fluorides. The behavior of $Mo^{99}F_6$ (Mo^{99} has a half life of 6.7 hr) in the sodium fluoride absorption step was in agreement with the results of other work on the MoF_6-NaF system. The disappearance of much of the radioactive iodine, tellurium, niobium, ruthenium, and molybdenum in the fused-salt dissolution step indicated that precipitation or volatilization and condensation at the top of the dissolution reactor occurred and that not much of the material was carried out of the vessel with the excess hydrogen fluoride.

Table III-1 FUSED-SALT VOLATILITY-PROCESS DISSOLUTION RUNS[1]

[Runs T-8 Through T-10: Zircaloy-2, ~30 Kg per Element, Two Elements per Run; Runs TU-8 Through TU-12: Nonirradiated Fully Enriched Zirconium-Uranium Alloy Fuel, ~1% Uranium, ~40 Kg of Fuel per Run; Runs R-1 Through R-6: 5.2 and 6.5-Year Decayed Enriched Zirconium-Uranium Alloy Fuel, ~25 Kg per Element; Initial Molten Salt: NaF (28 to 39 Mole %)–LiF (30 to 42 Mole %)–ZrF_4 (23 to 42 Mole %)]

Run No.	Salt temp., °C Max.	Salt temp., °C Min.	Av. dissolution rate,* kg/hr	Time,* hr	Av. HF flow rate, g/min	Av. HF utilization,* %
T-8	640	500	1.60†	23.2†	150	15.9†
T-9	560	510	2.90	11.0	190	22.3
T-10	640	490	2.75	17.5	162	25.8
TU-8	652	495	4.80	7.4	122	52.0
TU-9	665	480	2.70	14.1	180	20.6
TU-10	650	495	2.50	14.5	150	24.5
TU-11	665	495	2.30	16.0	150	23.5
TU-12	640	505	3.30	11.2	150	32.0
R-1	650	500	1.80	26.4	150	17.1
R-2	650	495	3.10	14.0	150	29.8
R-3	645	490	3.18	12.3	75–150	31.2
R-4	655	550	5.34	8.0	75–150	54.6
R-5	660	500	2.86	14.0	75–150	30.3
R-6	650	495	2.48	17.4	75–150	27.6

*Based on 90% completion of dissolution.
†Run terminated at 70% dissolution.

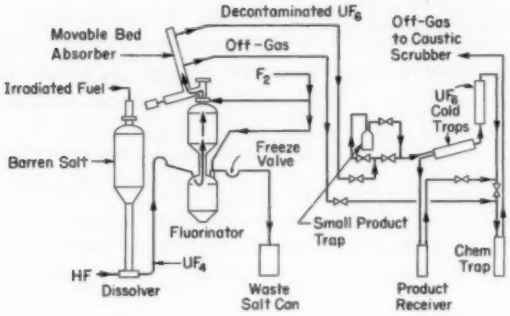

Fig. III-2 Uranium system of the ORNL Volatility Pilot Plant.[2]

Dissolution rates for the irradiated uranium dioxide clad in Zircaloy-2, used as feed material, were approximately the same as those which had been obtained with unirradiated material. Dissolution rates for the uranium dioxide pellets used here ranged from 8.2 to 16.5 mils/hr in the 31-24-45 mole % LiF-NaF-ZrF_4 salt at 650°C. In contrast, the average dissolution rates of the two zirconium alloy fuels, runs T-10 and TU-10 (reported in kilograms per hour in Table III-1), were each 3.6 mils/hr based on initial fuel-element area.

Absorption of Volatile Fluorides on Beds of Solid Fluorides. In previous absorption studies at ORNL, the equilibria of the systems UF_6-NaF and MoF_6-NaF were determined quantitatively. The absorption and retention of niobium on sodium fluoride has also been established in uranium decontamination experiments. From recent work[1-3] the following summary has been made regarding absorption on sodium fluoride of the pertinent contaminants forming volatile fluorides:

1. Iodine and tellurium fluorides are not absorbed on sodium fluoride at 100°C.
2. Ruthenium behavior appears anomalous; RuF_6 is probably not absorbed on sodium fluoride, but other ruthenium fluorides may behave differently.
3. Niobium, plutonium, chromium, and probably antimony fluorides form irreversible complexes with sodium fluoride.
4. Molybdenum, neptunium, and technetium fluorides absorb and desorb with uranium hexafluoride.

Vapor Pressure of Technetium Hexafluoride. Values of the vapor pressure and transition points of technetium hexafluoride have been reported by Selig and Malm of Argonne National Laboratory (ANL).[4] The technetium hexafluoride used in these determinations was produced by the reaction of fluorine and metal at 400°C. No other fluoride of technetium was detected, and the product was determined to be of high purity. The following equations summarize the vapor pressure results:

Solid I (– 16.32 to – 5.3°C):

$$\log p = \frac{-3564.8}{T} - 10.787 \log T + 41.1252$$

Solid II (– 5.3 to + 37.4°C):

$$\log p = \frac{-2178.0}{T} - 2.295 \log T + 15.33427$$

Liquid (+ 37.4 to 51.67°C):

$$\log p = \frac{-2404.9}{T} - 5.8036 \log T + 24.8087$$

with p = pressure (mm Hg) and T = temperature (°K).

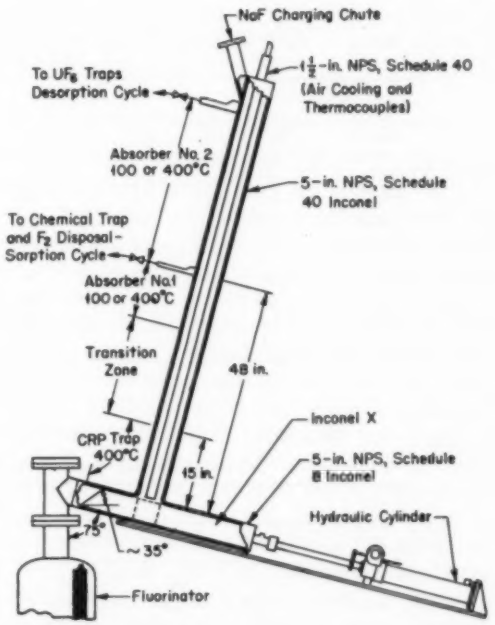

Fig. III-3 Movable-bed temperature-zoned sodium fluoride absorber.[2]

Table III-2 FUSED-SALT VOLTALITY-PROCESS FLUORINATION RUNS[1]

[Initial Molten Salt: NaF (28 to 37 Mole %)–LiF (20 to 40 Mole %)–ZrF_4 (38 to 40 Mole %); Fluorination Temperature: 495 to 515°C]

Run No.	Salt U conc., ppm		F_2 flow, standard liters/min	Fluorination time, min	F_2 utilization,* %	Mole ratio of F_2 used* to original U	Fluorination time to obtain 10 ppm U in salt, min	Total nonrecoverable U losses	
	Initial	Final						Grams	Wt.%
TU-8	2430	2.0	6	100	5.2	19.3	111	0.415	0.08
			16	20					
TU-9	2455	5.0	6	100	7.8	12.8	89	1.360	0.20
TU-10	2250	6.3	6	100	4.7	21.5	119	0.887	0.28
			14	23					
TU-11	3000	2.2	6	100	4.7	21.5	106	0.245	0.07
			14	20					
TU-12	2560	4.0	6	100	6.3	16.0	103	1.270	0.16
			14	20					
R-1	1473	12.5	6	101	~2.7			7.020†	2.20
			10	9					
			14	15					
R-2	2252	0.8	6	101	4.9	20.5	81	0.143	0.03
			14	19					
R-3	1564	7.3	6	202	1.5	69.0	240‡	1.438	0.45
			14	58					
R-4	938	3.0	6	101	3.6	27.9	94	0.681	0.32
			14	19					
R-5	1116	4.0	6	101	3.4	29.2	100	0.773	0.36
			13.4	19					
R-6	1400	0.8	6	101	2.2	46.2	134	0.134	0.06
			13	49					

*Based on time required to obtain 10 ppm uranium in waste salt.
†Loss due to excessive NaF discharge from temperature-zoned absorber.
‡Attributed to lower than normal fluorinator salt interface temperatures.

Table III-3 CATION IMPURITIES IN URANIUM HEXAFLUORIDE PRODUCT OF VOLATILITY PROCESS[1]

Run No.	Amount, ppm of UF_6												
	Cr	Cu	Fe	Li	Mo	Na	Ni	Sn	Zr	Np	Tc	Pu	Total
TU-8	<1	<1	<1	<1	100	12	15	<1	<1				<133
TU-9	<1	<1	<1	<1	19	10	14	<1	<1				<49
TU-10	188	1005	180	<5	23	440	910	460	24				<3235
TU-11	<1	1	<1	<1	47	420	3	<1	<1				<476
R-1	130	83	24	<1	32	155	52	<1	<1	157	<1	$<10^{-3}$	<637
R-2	12	12	40	<1	350	180	15	<5	<3	177	69	$<10^{-3}$	<864
R-3	<80	17	6	<1	130	96	1	<4	<4	8	59	$<10^{-3}$	<406
R-4	<1	27	13		560		<5	<10	<5	3	159		

Table III-4 URANIUM-RECOVERY-SYSTEM APPROXIMATE DECONTAMINATION FACTORS[1]

(Fuel: 5.2 to 6.5-Year-Decayed Enriched Zirconium-Uranium Alloy Fuel)

Run No.	Decontamination factors								
	Gross β	Gross γ	TRE β*	Cs^{137}	Ru^{106}	Zr^{95}	Nb^{95}	Sr^{90}	Sb^{125}
R-1	5×10^6	10^7	10^8	$\sim 5 \times 10^9$	$\sim 5 \times 10^5$	$\sim 5 \times 10^6$	$\sim 10^5$	$\sim 10^9$	$\sim 10^7$
R-2	5×10^6	10^8	10^{10}	$\sim 10^9$	$\sim 10^6$	$\sim 5 \times 10^5$	$\sim 10^6$	$\sim 5 \times 10^9$	$\sim 10^7$
R-3	10^6	5×10^7	$\sim 10^8$	$\sim 10^9$	$\sim 10^9$	$\sim 10^4$	$\sim 10^5$		$\sim 10^4$
R-4	10^6	10^8	$\sim 10^9$		$\sim 10^5$				$\sim 10^6$

*TRE = total rare earths.

The calculated values of the triple point and the boiling point are 37.3 and 55.3°C, respectively. The Trouton constant[4] for the liquid is 22.0 cal/(gram mole)(°K).

Dry Halogenation Processes

A fluidization-volatility process scheme for the recovery of uranium from enriched uranium-zirconium alloy nuclear fuels is being studied at ANL.[5] The process involves reaction of the alloy with hydrogen chloride gas while the uranium-zirconium fuel is submerged in an inert fluidized bed of Alundum particles. During the reaction of the alloy with hydrogen chloride, the zirconium is sublimed as the tetrachloride, leaving particulate uranium trichloride in the reactor assembly. Uranium is recovered as volatile uranium hexafluoride during a subsequent fluorination step.

Recent studies[5] in a $1\frac{1}{2}$-in.-diameter fluid-bed reactor have been concerned with the effect of hydrogen chloride excess and reaction temperature during hydrochlorination of the alloy on the overall retention of the uranium in the fluid bed of Alundum after fluorination. Results showed that the lowest residual uranium content was associated with the utilization of large amounts of hydrogen chloride (11 to 25 times the stoichiometric requirement) and high temperatures (500 to 550°C). The range of uranium values in the bed after fluorination extended from only 0.03 to 0.06 wt.%. This was equivalent to a retention of from 0.8 to 1.9% of the initial uranium charged. Increased uranium removal from the bed was achieved by refluorination of the bed material at 500°C after an initial fluorination period at 400°C. Results of runs in which only four times the stoichiometric equivalent of hydrogen chloride was utilized indicate that this is an inadequate amount since concentrations of residual zirconium in the bed were relatively high, 0.23 to 0.44 wt.% of the bed, compared with 0.04 wt.% when large hydrogen chloride excesses were used.

The use of phosgene gas to treat the residue remaining in the fluid bed after reaction with hydrogen chloride resulted in very low residual uranium values (less than 0.01 wt.% of the final bed, equivalent to < 0.2% of the uranium charged). These tests were performed using a gas mixture containing 50 vol.% phosgene in nitrogen at a bed temperature of 400°C for a period of from 3 to 5 hr.

Table III-5 URANIUM PRODUCT SUMMARY[2]

	Cation impurities, ppm of U								Activity, counts/(min)(mg of U)	
	Cr	Li	Mo	Tc	Np	Pu	Other cations	Total	Gross β	Gross γ
AEC specification*	< 200	< 10	< 200			< 1 ppb		< 300	195	9
Returned product (Runs TU-8 to TU-11)	130	< 1	94				140	365		
Returned product (Runs R-1 to R-4)	< 1	< 1	777	121	2	< 1 ppb	145	1050	360 ± 90	8 ± 1

*Federal Register, 25: 2817 (Apr. 2, 1960) (for enriched UF_6 returned to AEC).

Uranium Separation from Other Elements in UO_2 Fuels

A method for separating uranium from certain other elements which may be present in uranium dioxide fuels has been described by Ishihara and associates.[6] This method is based on volatilization of chlorides and selective condensation of uranium tetrachloride at a temperature depending principally on the properties of the chloride formed from the oxides associated with the uranium dioxide feed materials. Process conditions were established by reacting, in turn, powdered mixtures of UO_2-ZrO_2, UO_2-MoO_3, UO_2-CeO_2, and UO_2-ThO_2 with carbon tetrachloride at 500°C. Separation of uranium from UO_2-CeO_2 and UO_2-ThO_2 mixtures was readily achieved since the chlorides of cerium and thorium are relatively nonvolatile. Approximately 95 to 98% of the uranium was collected in high purity in condensers operating at 30°C. Separation from molybdenum was effected by condensing uranium tetrachloride at 200°C. Molybdenum pentachloride, boil-

ing point 268°C, was identified as the volatile chloride produced in the reaction between molybdenum trioxide and carbon tetrachloride. It was not possible to achieve a complete separation of uranium by selective condensation during chlorination of UO_2-ZrO_2 mixtures.

Direct Fluorination Processes

A direct fluorination volatility process is being developed at ANL[5] to recover uranium and plutonium from spent uranium oxide fuel elements that are clad with Zircaloy or stainless steel. The proposed process involves decladding of the spent uranium dioxide fuel by an appropriate reaction in a fluidized bed. Plutonium and uranium hexafluorides, which result from the reaction of the declad oxide fuel with fluorine, are to be separated from volatile fission products by distillation and are to be separated from one another by thermal decomposition of the plutonium hexafluoride.

The direct fluorination of uranium dioxide pellet fuel is being studied on an engineering scale in a 3-in.-diameter air-cooled reactor with the aim of optimizing reaction rate, fluorine efficiency, and fluidization quality. The technique of fluidization of inert, refractory alumina (Alundum) in the voids of the uranium dioxide pellet bed is used as an aid to heat removal. Two recent tests have been made at 500°C with a total fluidization velocity of 1.3 ft/sec and an initial pellet bed 18 in. deep (13.2 kg of uranium dioxide). These runs employed a partial recycle of process gas to promote fluorine utilization efficiency while maintaining a predetermined low concentration of oxygen entering the reactor. In one run made at a relatively low uranium hexafluoride production rate [17 lb of UF_6/(hr)(sq ft)], the fluorination was carried to completion in 44 hr with good fluidization and 78% overall fluorine efficiency. In a second run made at a fluorination rate about 30% higher, operating instabilities developed with respect to gas channeling and bed caking. These results suggest that a bed of uranium dioxide pellets having the geometry used in these runs can be fluorinated only at a moderate rate corresponding to a process time of about 40 hr.

Another aspect of the development of the same process at Argonne[5] involves a study designed to elucidate the factors involved in the removal of plutonium by fluorination from powder mixtures of Alundum, uranium dioxide, and plutonium oxide. This is important in establishing the conditions necessary for minimum loss of plutonium in the granular Alundum which is intended to be used in the process as a fluidized heat-transfer medium. Small-scale laboratory experiments were carried out using an initial mild fluorination step employing 10 vol.% fluorine at 450°C. This initial step was followed by a second fluorination using 75 vol.% fluorine at 550°C or at 650°C. The lowest plutonium concentration in the Alundum residue, obtained in two experiments in which the second fluorination was performed at a temperature of 650°C for 5 hr, averaged 0.016 wt.%, which corresponded to a removal of 98.7% of the initial plutonium.

Table III-6 ACTIVITIES IN URANIUM HEXAFLUORIDE PRODUCED IN LABORATORY-SCALE FLUORIDE-VOLATILITY TESTS WITH SHORT-DECAYED URANIUM DIOXIDE FUEL[1,3]

	(Counts per minute per milligram of uranium)$_{\text{fission products}}$ /(counts per minute per milligram of uranium)$_{\text{natural U}}$*												
										Calculated total fission products			
Run No.	Zr γ	Sr β	Ba β	Cs γ	Ru γ	Nb γ	I γ	Te β	Mo β	Gross β	Gross γ	U^{237} β	U^{237} γ
1		0.45		<0.1	22	13	12	$<10^{-2}$	56	56	47	2.5×10^3	1.6×10^3
2	1.3	9.0×10^{-2}	$<10^{-2}$	1.9	<0.1	3.4	3.8	$<10^{-2}$	48	48	10	1.2×10^3	7.8×10^2
3	28		$<10^{-2}$		<0.1	23	1.3	4.1×10^{-2}	3.2	3.2	52	4.1×10^3	2.9×10^3
4	8.0	2.1×10^{-3}	$<10^{-2}$		<0.1	2.2	21	5.9×10^{-3}	70	70	31	3.0×10^3	2.1×10^3
5	0.55	$<10^{-2}$	2.4×10^{-3}		0.26	2.6	120	1.9×10^{-3}	12	12	124	1.6×10^3	9.8×10^2
6	1.5	5.5×10^{-3}	$<10^{-2}$	1.1	2.6	19	16	7.5×10^{-2}	9.2	9.2	40	9.0×10^2	6.4×10^2

*Natural-uranium activity is taken as 80 β counts/min and 8 γ counts/min per milligram of uranium.

An important variable in the reaction scheme was the quantity of refractory alumina used as the inert solid. A series of experiments was performed in which the amount of Alundum was varied while the amount of uranium-plutonium oxides was kept constant, as were the reaction conditions (fluorination at 450°C followed by fluorination at 550°C). As the percentage of Alundum in the mixture was increased from 21 to 30 to 47%, the percentages of the total plutonium removed from the mixtures decreased from 95 to 87 to 77%, respectively. Two tests were performed to determine the feasibility of using the same batch of alumina for several fluorinations, with new batches of uranium-plutonium oxides added prior to each fluorination. The recycle use of alumina did not result in a greater removal of plutonium than would have resulted if three separate batches of alumina had been used.

Preparation and Properties of Fluorides

The reactions of the hexafluorides of molybdenum, tungsten, and uranium with nitrous oxide and nitric oxide have been studied by Geichman and associates.[7] Experimental conditions were 200 mm total pressure, temperatures of 25 or 60°C, and reaction times of 4 to 24 hr. The reaction of nitric oxide with molybdenum hexafluoride and uranium hexafluoride gives the solid ionic compounds, $NO^+(MoF_6)^-$ and $NO^+(UF_6)^-$. These same compounds result when molybdenum pentafluoride and uranium pentafluoride are allowed to react with nitrosyl fluoride. No reaction occurs between nitric oxide and tungsten hexafluoride. Nitrous oxide does not appear to react with tungsten, molybdenum, or uranium hexafluorides.

Malm and Selig at Argonne[8] investigated the reaction between sodium fluoride and uranium hexafluoride and reported the formation of the compound $NaUF_7$. The reaction was studied with the sodium fluoride suspended in the fluorocarbon C_7F_{16} in order to remove rapidly the heat of reduction resulting from the interaction between sodium fluoride and uranium hexafluoride. At 100°C the reaction goes rapidly to completion to form $NaUF_7$, which has a dissociation pressure of 35 mm at 100°C. On heating $NaUF_7$ at 100°C under vacuum, the material evolves uranium hexafluoride to produce Na_2UF_8. This compound, when heated to 300°C, rapidly gives off uranium hexafluoride according to the reaction

$$Na_2UF_8 \rightarrow 2NaF + UF_6$$

Similar studies with potassium fluoride showed that analogous compounds are formed.

A comprehensive review of the properties of hexafluoride molecules has been published by Weinstock.[9] Another review article[10] has been published which covers most of the available literature on the chemistry of uranium fluorides.

Hubbard has published a detailed description[11] of the experimental apparatus and procedures used in performing fluorine bomb calorimetric determinations. The heats of formation of titanium tetrafluoride and hafnium tetrafluoride have been recently reported by Hubbard and associates.[12] These data were obtained by direct combination of the elements in a combustion bomb calorimeter. Armstrong and Krieger[13] have published the results of a survey of the recent literature on the thermochemical properties of inorganic fluorine compounds. The authors include a bibliography of 625 references to the literature.

Claassen and others at Argonne[14,15] have discovered that the rare gas xenon reacts with fluorine to give a solid compound, XeF_4, that is stable at room temperature. This compound is the first xenon molecule having four bonds and containing only one other element. Complete reaction of xenon with fluorine is achieved by heating one part xenon and five parts fluorine (by volume) to 400°C for 1 hr. The vessel is cooled rapidly to room temperature, and the excess fluorine is removed at −78°C. Xenon tetrafluoride forms as colorless crystals with a negligible vapor pressure at −78°C. The compound melts at about 90°C.

Pure vanadium tetrafluoride has been prepared by the reaction between vanadium tetrachloride and hydrogen fluoride.[16] Vanadium tetrafluoride may also be prepared from the metal and gaseous fluorine. The tetrafluoride is thermally unstable; at 100 to 120°C in a vacuum, it disproportionates into vanadium trifluoride and vanadium pentafluoride. Vanadium tetrafluoride is readily converted into vanadium pentafluoride by bromine trifluoride and fluorine. The tetrafluoride is much less

reactive than the pentafluoride, as shown by the lack of reaction with sulfur dioxide or sulfur trioxide, both of which are fluorinated by the pentafluoride.

Pyrometallurgical Processes

Pyrometallurgical processes for recovery of discharged reactor fuel material include processes in which fuel materials are processed directly as metals and those processes in which both metal and ceramic fuel materials are processed in liquid metal–salt solvent systems. The incentive for development of pyrometallurgical processes stems principally from economies that are expected to be derived from the capability of such processes for handling short-cooled fuels with an attendant reduction of fuel inventories and from avoidance or simplification of chemical conversions. Pyrometallurgical processes are not generally high decontamination processes, and their development must therefore be accompanied by a parallel development of methods for remote refabrication of reactor fuel elements.

Melt Refining

As reported in the most recent progress report of the Argonne Chemical Engineering Division,[17] progress continues to be made in preparing the Experimental Breeder Reactor No. 2 (EBR-II) fuel-cycle facility for processing discharged fuel from the EBR-II reactor. The melt-refining process, a simple melting process in which fission products are removed by volatilization and selective oxidation reactions, will be employed to recover and purify the discharged fuel. Its use will constitute the first large-scale demonstration of a pyrometallurgical process. With the exception of some corrective work, construction of the fuel-cycle facility is essentially complete.[17] Installation of processing equipment has been started.

One-thousand-watt mercury-vapor lamps with white phosphor-coated soft-glass envelopes are to be used to illuminate the processing cells of the fuel-cycle facility.[17] Although the effects of radiation on the lumen output of the 1000-watt lamps had previously been determined,[18] little was known about the effects of lamp life, lamp voltage, and ambient temperature on lumen output. Information on these effects has been obtained[17] in a mockup lighting installation that has been in service for $3\frac{1}{2}$ years. Of the nine original lamps that were installed in the mockup installation, seven are still in operation after 6000 hr of use. The other two lamps burned out after approximately 300 hr of service. The lumen output for the seven lamps still in use decreased to about 70% of the initial output, with much of this decrease occurring during the first 1000 hr of use. Other conclusions are that (1) a line voltage variation of 1% should affect the illumination by not more than 2% and (2) an increase in the ambient temperature from 25°C to 40°C (the expected ambient temperature of the fuel-cycle facility) should cause no more than a 10% decrease in light output.

A series of small-scale high-activity-level melt-refining experiments, which constitute final demonstrations of the melt-refining process, has been in progress at ANL (see previous Reviews).[19,20] The fifth and final experiment has been completed.[17] A 382-g charge of EBR-II prototype fuel (10% enriched uranium alloyed with 5% fissium) irradiated to 2 at.% total burnup and cooled 25 days was melt refined for 1 hr at 1400°C. The yield of purified metal was 73%. In these runs the yields have generally been about 72%, as compared with 85% yields obtained in similar runs with unirradiated fuel. (At the full-process scale of 10 kg, yields are expected to be 90 to 95%.) After consideration of all the information available on these runs, the reduced yield with irradiated material appears to result from increased oxidation of the irradiated fuel pins during necessary exposure to air prior to melt refining. Since air exposure can be avoided in the argon cell of the EBR-II fuel-cycle facility, reduced yields resulting from irradiation of the fuel are considered unlikely.

An investigation was completed on the behavior of iodine during off-gas handling operations that follow melt refining of highly irradiated EBR-II fuel.[17] The argon atmosphere of the melt-refining furnace and the fission-product gases released during melt refining are to be pumped through an iodine trap to an exterior storage tank from which they may be vented through a stack when meteorological conditions are favorable. It was found that about 10^{-3}% (an order of magnitude value) of the iodine present in the initial charge was removed from the melt-refining furnace on pumping it down to a

final pressure of 8 mm Hg while the melt-refining crucible was at a temperature of 650°C. The iodine trap, which was located between the pump and furnace, consisted of a bed of activated charcoal, with AEC filters at the fore and aft sides of the charcoal bed to remove particulate activity from the gas stream. The trap removed essentially all the iodine activity from the gas stream and retained it at the low (8 mm) pressure existing in the final stage of the furnace pumpdown. The effluent from the iodine trap contained 10^{-8}% or less of the iodine present in the furnace gas. A small fraction (a few tenths of 1%) of the rare-gas activity in the off-gases was also retained by the charcoal bed.

Because the argon atmosphere of the fuel-cycle facility may contain as much as 5% nitrogen, it is important to know the extent of nitridation of irradiated EBR-II uranium-fissium alloy pins in this atmosphere and the conditions under which ignition of the irradiated pins will occur. Self-heating resulting from nitridation of single uranium-fissium pins was found to begin at 660°C in 5% nitrogen and 100% nitrogen and at 730°C in 1% nitrogen but did not occur on heating a pin to 920°C in 0.5% nitrogen.[17] At the higher nitrogen concentrations, the ignition temperature may be related to the rapid swelling of irradiated fuel pins, which begins between 600 and 700°C. These results indicate that ignition can be avoided by keeping the fuel temperatures below about 600°C or by reducing the nitrogen concentration below about 0.5%.

In separate experiments with unirradiated fuel pins,[17] the extent of pin nitridation occurring during storage of the fuel pins for 2 hr at 650°C in a 5% nitrogen–argon atmosphere was found to have a negligible effect on melt-refining yield. The storage conditions employed simulate those expected for fully irradiated fuel pins in the EBR-II fuel-cycle facility, except that effects of irradiation (e.g., swelling of pins due to the presence of fission gases) were absent.

Fundamental Studies of Liquid-Metal and Salt Systems

Solubilities in Liquid-Metal Systems. For the design of processes utilizing liquid-metal systems, it was necessary to obtain the solubilities of fission-product elements, fissionable

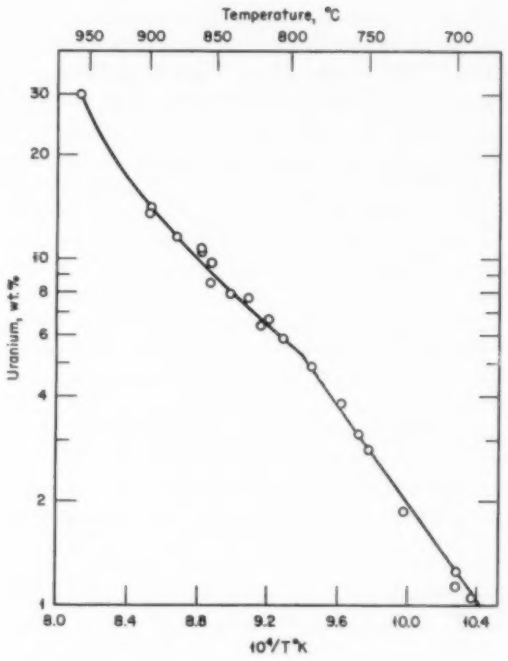

Fig. III-4 The zinc-rich liquidus in the zinc-uranium system.[17]

elements, and structural elements in liquid-metal solvents. The solubilities of the long-lived fission products in bismuth have been reported[21] for temperatures ranging from 300 to 700°C. Solubility curves as a function of temperature are given for strontium, barium, yttrium, lanthanum, cesium, praseodymium, neodymium, samarium, germanium, zirconium, molybdenum, technetium, ruthenium, and palladium.

Other new solubility data that have been reported are (1) the solubility of strontium in liquid zinc,[17] which may be represented for the temperature interval of 506 to 727°C by the following equation: log (at.% strontium in zinc) = $9.619 - 9940\,T^{-1}$ (T in °K), and (2) some additional measurements of the solubility of uranium in zinc.[17] A plot of the new uranium solubility data together with older data[22] is shown in Fig. III-4. These latter data are important to pyrometallurgical process applications because zinc is commonly used as a solvent for uranium.

The liquidus uranium concentration in the uranium-bismuth system[23] was found to be

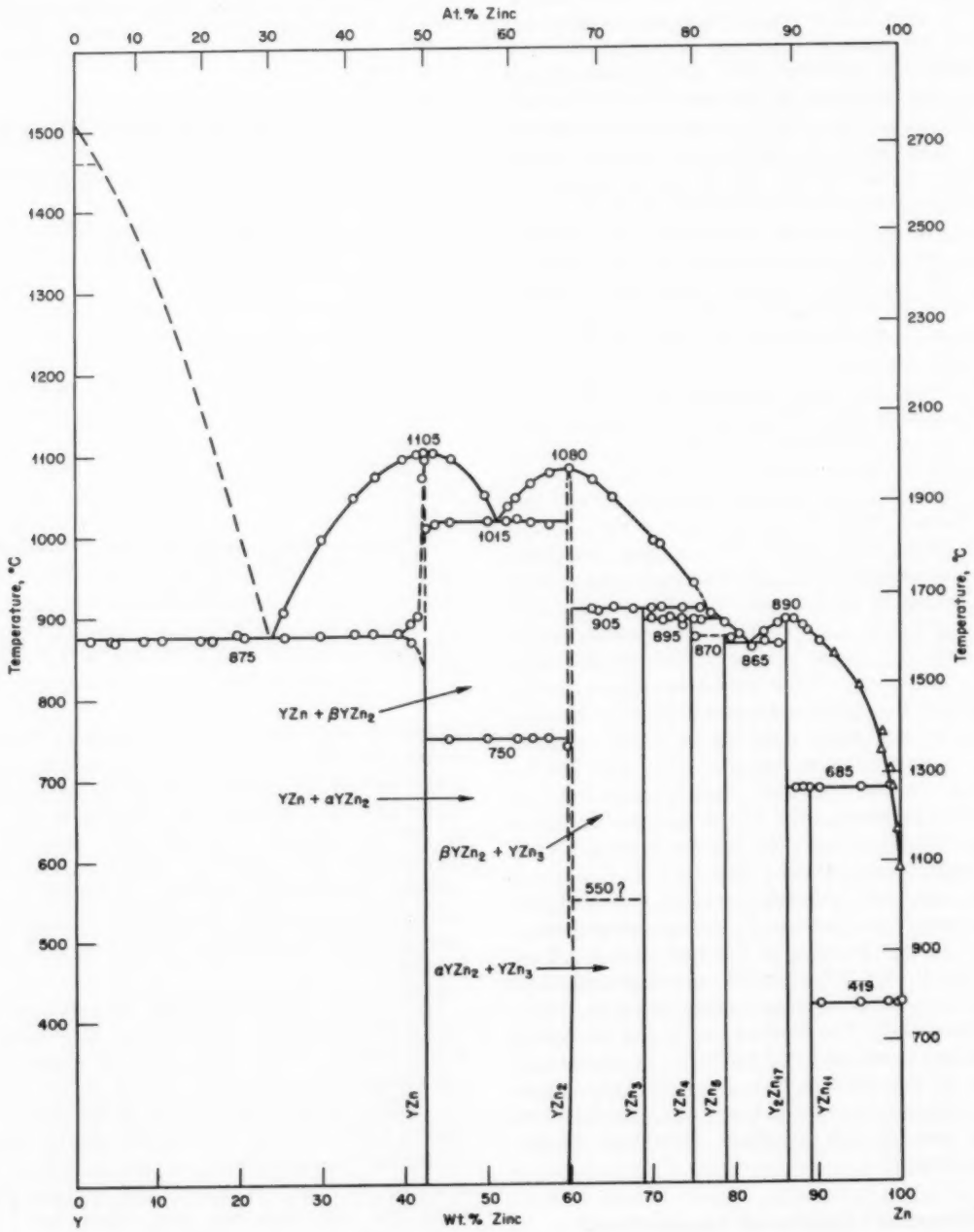

Fig. III-5 Phase diagram for the yttrium-zinc system under constrained vapor conditions.[25]

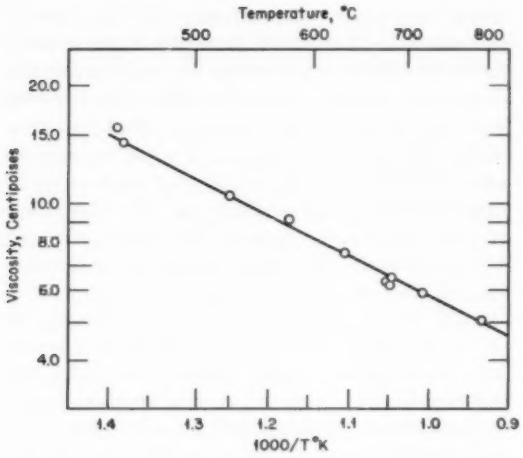

Fig. III-6 Viscosity of plutonium-cerium-cobalt eutectic alloy as a function of absolute temperature.[32] Alloy composition is 19.6% plutonium–24.2% cobalt–56.2% cerium.

represented by the following equation for the temperature range 400 to 800°C: log (wt.% uranium) = $3.272-2690T^{-1}$ (T in °K). On the basis of this equation, the partial molar enthalpy change for the reaction

$$UBi_2 \rightarrow U + 2Bi$$

was calculated to be 12,300 cal/gram mole. Addition of copper to the uranium-bismuth system produced a continuous decrease in the uranium concentrations at liquidus. Addition of palladium to the bismuth-uranium system at concentrations of less than 0.6 wt.% had no effect on the uranium liquidus, but, at palladium concentrations above 0.6%, the uranium solubilities were sharply depressed.

Phase Diagrams and Thermodynamic Properties of Intermetallic Compounds. The utility of solubility data is increased considerably by knowledge of phase diagrams and of the properties of the solid and liquid phases. The existence of two intermetallic phases in the uranium-zinc system was reported in a previous Review.[24] One of the intermetallic phases, the epsilon phase, does not have a fixed composition, but rather a composition range in the vicinity of U_2Zn_{23}. The other intermetallic phase, which has been designated as the delta phase, has been identified as U_2Zn_{17}. The break in the uranium solubility curve shown in Fig. III-4 indicates the decomposition temperature of the epsilon phase[17] to be about 790°C. The products of this peritectic decomposition are the delta phase and melt saturated with uranium.

Work at Ames Laboratory on the yttrium-zinc system has been completed.[25] The phase diagram for this system, shown in Fig. III-5, may be compared with an earlier version.[26] The standard free energies of formation of the yttrium-zinc compounds were derived from vapor pressure measurements, and other thermodynamic quantities (enthalpy and entropy) were calculated.[25] A report has also been issued on the determination, from vapor pressure measurements, of thermodynamic functions for the formation of binary intermetallic phases.[27] The phase diagram of the vanadium-zinc system has been reported by ANL.[17] Also reported by ANL is the identification by a vapor effusion method of the intermetallic phases in the lanthanum-zinc system.[17] Some revisions in the plutonium-aluminum phase diagram have been disclosed by investigators at Los Alamos Scientific Laboratory.[28] Preliminary information on the plutonium-cerium phase diagram is also available.[29,30]

Properties of Metal Systems. An empirical relation between the activation energy of viscosity for many liquid metals and their melting points has been developed[31] using data in the literature.

Viscosities are among the physical properties of plutonium-bearing fuel materials which are under measurement at Mound Laboratory. Viscosity of a 19.6% plutonium–24.2% cobalt–56.2% cerium alloy as a function of temperature[32] is shown in Fig. III-6. The density of this plutonium-cobalt-cerium alloy,[32] which is shown in Table III-7, is only 3% greater than the value calculated from the gram-atomic volumes occupied by the individual constituents. The density of the molten plutonium-iron eutectic has also been measured.[29] A method for the investigation of specific volumes and densities of liquid metals and alloys has been published[33,34] and was employed for determinations of the densities of aluminum, tin, and bismuth.

The determination of diffusivities of uranium in various liquid-metal solutions, in progress at ANL, was recently extended to a determination of the diffusivity of uranium in bismuth.[17]

Table III-7 DENSITY OF PLUTONIUM-CERIUM-COBALT ALLOY[32]

(Composition: 19.6 Wt.% Plutonium, 24.2 Wt.% Cobalt, and 56.2 Wt.% Cerium)

Temp., °C	Density, g/cm^3
753	8.909
528	8.956
474	8.976

The diffusivity values varied from 2.5×10^{-5} cm^2/sec at 500°C to 4.6×10^{-5} cm^2/sec at 725°C. As in other systems that have been studied (uranium-cadmium and uranium-zinc), the diffusivities in bismuth are below those calculated by the Einstein-Stokes equation. This suggests partial ordering of solvent atoms around uranium atoms.

Distribution of Elements Between Immiscible Phases. The distribution of solute elements between immiscible phases can be used as the basis of solvent-extraction processes for the separation of various solute elements. Distributions of fission-product elements and plutonium between liquid-metal and salt phases are being studied at ANL for application to the purification of plutonium fuels — in particular, separation of plutonium from rare-earth elements. Plutonium-containing fuels will be used at some time in the future in the EBR-II reactor. Distribution coefficients are being determined, for elements of interest, between molten magnesium-zinc alloys and molten magnesium chloride. Distribution data for this system previously reported in another Review[35] showed uranium and plutonium to distribute preferentially into the metal phase and showed yttrium, cerium, praseodymium, and samarium to distribute preferentially into the flux phase. Recent additions to these data[17] showed that thorium, vanadium, and zirconium tend to favor the metal phase, whereas barium appears only in the flux.

For the same system, measurements have also been made of the effects of plutonium and uranium concentrations on their distribution coefficients.[17] The distribution coefficient (weight percent in flux/weight percent in metal) for uranium at 10 wt.% magnesium in the metal phase increases with increasing uranium concentration in the metal phase up to about 2 wt.%. Above 2 wt.% uranium the distribution coefficient increases only slightly. In the case of plutonium, only a slight increase in the distribution coefficient was found on increasing the plutonium concentration in the metal phase from 0.5 to 4.8 wt.%. The key plutonium–rare earth element separation, i.e., the separation most difficult to effect, is the separation of plutonium from praseodymium. The logarithm of the separation factor for plutonium and praseodymium* increased linearly as a function of the reciprocal absolute temperature. At 850°C the separation factor was 25; at 620°C it was 47. When the magnesium chloride flux was diluted with lithium chloride, the distribution coefficients for plutonium and praseodymium both decreased gradually at first, then dropped off sharply as the magnesium chloride concentration was reduced below about 30 mole %. Substitution of cadmium for zinc in the metal phase had little effect on the distribution coefficients of plutonium and praseodymium.

Molten-salt extraction is being investigated at Ames Laboratory as a means of separating uranium from thorium when both are present in an aluminum alloy (aluminum–25% thorium alloy containing approximately 0.25% uranium).[36] After the molten aluminum alloy was equilibrated with a molten potassium chloride–aluminum chloride salt, distribution coefficients for thorium (grams of thorium per gram of salt/grams of thorium per gram of metal) were found to be 55 to 65 times greater than those for uranium. In this extraction, aluminum chloride is reduced by thorium. The salt composition was adjusted to give a final mole ratio of potassium chloride to aluminum chloride of near 1, since work of Moore and Lyon[37] showed that, at this mole ratio, oxidation and extraction of uranium from a metal phase was greatly repressed whereas that of thorium was not much affected. Although this procedure would have the drawback for process application that the bulk component, thorium, rather than the desired uranium is preferentially extracted, the data are of interest. Other salt systems are being investigated in an attempt to obtain preferential extraction of uranium. Unfavorable uranium distribution coef-

*A separation factor is the ratio of two distribution coefficients. In this case it is the distribution coefficient of praseodymium divided by the distribution coefficient of plutonium.

ficients in favor of the salt phase have been obtained with the first alternative system investigated (lithium chloride–thorium chloride systems of various compositions).

A report[38] has been issued by Voigt and others at Ames Laboratory on the extraction of plutonium from molten uranium with the following relatively immiscible molten metals: silver, lanthanum, and cerium. Some of these data were reported in a previous Review.[39] For initial plutonium concentrations in uranium of 0.2%, distribution coefficients, defined as (grams of plutonium per mole of extractant/grams of plutonium per mole of uranium), were found to be 14 ± 1 for silver, 0.4 for lanthanum, and 0.5 for cerium. In these extractions, temperature variations within the range of 1175 to 1380°C had only a slight effect on the distribution coefficients. Plutonium distribution concentrations in the silver-uranium system were sensitive to the initial concentration of plutonium in uranium, increasing from 2.1 for an initial plutonium concentration of 0.0018% to 14 for an initial concentration of 0.2%. No such dependence on plutonium concentration was observed in the uranium-cerium and uranium-lanthanum systems. The plutonium distribution coefficients obtained in the uranium-cerium and uranium-lanthanum systems agree with those obtained by another investigator, McKenzie,[40,41] but those obtained in the silver-uranium system are considerably higher than those obtained by McKenzie. It is believed by the Ames investigators that the lower values obtained by McKenzie in the silver system were caused by his use of the entire uranium phase for analysis, which resulted in the inclusion of slagged plutonium that accumulates at the metal interface and along crucible surfaces.

Reduction of Compounds in Liquid-Metal Systems. The ability to reduce compounds, particularly those of uranium, thorium, and plutonium, in liquid-metal systems is important in several pyrometallurgical processes. In a continuation of work that is under way at ANL on the reduction of thorium oxide by magnesium-zinc alloy systems (generally containing about 5% magnesium), the effect of flux composition has been redefined using an argon atmosphere instead of an air atmosphere.[17] The flux composition range in which satisfactory reduction takes place with calcium chloride–magnesium chloride–calcium fluoride fluxes is greatly increased by the use of the inert atmosphere. At the optimum fluoride anion concentration of 10 at.%, only 10 or 11 at.% magnesium cation is needed to achieve complete reduction of thorium dioxide. A study of other variables involved in the reduction reaction showed that mixing speeds over 700 rpm were required for the scale and configuration of the laboratory equipment used and that the reduction rate increases as the temperature is raised. A temperature of about 800°C is considered to be optimum for process use.

Equilibrium studies in the reduction of thorium oxide by aluminum have been reported by Raleigh[42] (see also a previous Review[43]). In these studies thorium-aluminum melts were equilibrated with various molten fluoride salts that were saturated with thoria and alumina (solid excesses of both were present). The primary driving force for the reduction reaction was concluded to be the free energy of formation of $ThAl_3$, which was estimated to be −36 kcal/mole.

At Ames Laboratory, high-purity thorium is being prepared by reduction of purified thorium tetrachloride by magnesium to form a thorium–20 wt.% magnesium alloy which is later retorted to drive off the magnesium.[25,36,44] Reductions are performed at 965°C in an inert atmosphere in the presence of a magnesium chloride flux. After cooling and after physical removal of the solidified flux, the magnesium is removed by heating *in vacuo* at 350, 550, and 750°C for 2 hr each and finally at 920°C for 24 hr. Ninety-five percent overall yields of bright, clean thorium sponge have been obtained. Various methods of consolidating the sponge are being investigated, and these involve the use or combinations of arc melting and electron-beam melting. The preparation of magnesium-thorium as well as magnesium-zirconium alloys by reduction of the corresponding tetrachlorides under salt fluxes at 700 to 800°C has also been reported by Beyer and Seliger,[45] along with an evaluation of the physical properties of the products. The electrical resistivity of solid and molten thorium-magnesium eutectic alloys has been published.[46]

Cathode processes are being investigated by the Russians in connection with the preparation of thorium-zinc alloys in an electrolytic cell.[47,48] Characteristics of various electrolytes have been reported.

Reduction of uranium chloride by an amalgam-metallurgical process has been described in a German article.[49] In this process sodium amalgam is used to reduce uranium chloride (produced from uranium oxide by chlorination and reduction reactions) to produce a uranium amalgam. With good mixing the reaction is more than 90% complete after 4 hr at 300°C. Subsequently excess mercury is separated from the uranium amalgam by filtration, and the remaining mercury is distilled off in vacuum. By a special smoldering technique, uranium products containing less than 6 to 7 ppm mercury have been obtained. Economic estimates applicable to German operations indicate that the cost of producing uranium by the amalgam process would be 10 to 20% lower than the cost using present processes.[50]

Development of Liquid-Metal and Salt Processes

Processes that utilize molten metals and salts as processing media are currently under development at several atomic energy sites. Processes of this type are to be used by ANL (1) for the recovery of the skull or residue material remaining in a zirconia crucible after melt refining of fuel discharged from the EBR-II reactor and (2) for the enrichment of plutonium bred into the depleted uranium blanket material of the EBR-II. Flow sheets for these processes are given in the preceding Review.[51] Progress in the development of these processes is reported in a recent progress report of the Chemical Engineering Division.[17] The skull reclamation process is being developed and demonstrated on a 130-g uranium scale, and, at the same time, construction has begun on large-scale integrated equipment (approximately one-half plant scale) for further demonstration of the skull reclamation process.[17]

A recently declassified Hanford report[52] describes the purification of aluminum-U^{233} alloy fuel material which may be achieved by contacting the molten fuel material with a salt mixture of potassium and aluminum chlorides. Thorium-228, a radioactive daughter of U^{232}, is preferentially extracted into the salt phase, thus breaking the decay chain by which hazardous U^{232} daughter activities are produced. The salt phase may be used several times before it must be discarded. The U^{232} is produced (in small amount) with U^{233} in the thorium fuel cycle. Removal of the gamma-emitting daughter products would permit handling the uranium for a limited period of time with minimal shielding requirements.

Pyrometallurgical processes are surveyed along with aqueous and fused fluoride processes for the processing of thorium reactor fuels.[53] Limitations, advantages, and the status of the various processes are discussed.

Patents have been issued on the following pyrometallurgical processes:

1. Separation of uranium in a uranium-zirconium alloy from the zirconium by contacting with molten aluminum[54] at 800 to 900°C. Uranium dissolves in the aluminum while zirconium precipitates as a zirconium-aluminum intermetallic compound.
2. Separation of uranium from fission products by dissolving both in molten aluminum[55] and subsequently treating with hydrogen at between 200 and 300°C to form uranium hydride. Final separation is by mechanical means.

Construction Materials

Tungsten, tungsten alloys, and beryllia are the most promising materials for containment of the molten flux and metal systems to be used in the Argonne skull reclamation and blanket processes for the EBR-II fuel cycle. Pressed-and-sintered tungsten, rolled tungsten, and a molybdenum–30 wt.% tungsten alloy subjected to noble-metal extraction conditions (i.e., contacted with zinc and a halide flux composed of 47.5 mole % $CaCl_2$, 47.5 mole % $MgCl_2$, and 5 mole % MgF_2 at 800°C) for 400 or 500 hr underwent no detectable change in dimension.[56] Under the above conditions no corrosion of pressed-and-sintered tungsten specimens or of rolled tungsten specimens was detectable by metallographic examination, and the rupture strength of the specimens was not affected. Pressed-and-sintered tungsten crucibles will probably be used in processing the first EBR-II fuel loading. The molybdenum–30 wt.% tungsten specimens were attacked to a depth of 2 to 8 mils and showed a slight decrease in strength. This alloy is nevertheless considered satisfactory for such applications as agitators and transfer lines.

Thixotropically cast beryllia crucibles have shown excellent performance as containers for the last three steps of the skull reclamation

process (two precipitation steps and a retorting step in molten magnesium-zinc media).[17] In tests of two such crucibles, no significant change could be detected in the crucibles, one of which was jacketed in stainless steel and one of which was unjacketed, after each had been exposed to process systems for about 180 hr. During this time the systems were thermally cycled 10 to 20 times between 450 and 800°C. Work is beginning on the development of fabrication methods and materials for large-size ceramic containers.

Studies of Additional Corrosion-Resistant Materials

Tantalum and tantalum alloys are being used and tested for containment of the first Los Alamos Molten Plutonium Reactor Experiment (LAMPRE) core loading, a high-purity liquid plutonium–10 at.% iron alloy. The alloys under test are (1) electron-beam-melted pure tantalum, (2) double-arc-melted pure tantalum, (3) tantalum–0.1 wt.% tungsten, and (4) tantalum–0.75 wt.% tungsten–0.2 wt.% yttrium.[57] Test temperatures employed were 625, 675, 700, and 725°C with times at each temperature of up to 2100 hr. Of 36 containers tested, none failed at 625°C. At 675°C pure tantalum was superior to the tungsten-containing alloys in withstanding intergranular penetration. On the basis of these tests, future capsules will be fabricated from unalloyed tantalum, and wall temperatures will be limited to 625°C.

Studies of a plutonium-cobalt-cerium fuel alloy (composition not stated) contained in tantalum have shown that a reaction layer, tentatively identified as TaCo, forms on the container wall.[57] Since plutonium-cobalt-cerium alloys are being considered for use in a direct-contact core, i.e., a core in which sodium coolant is in contact with the molten fuel alloy, compatability studies between these alloys and sodium have been carried out. In one test, sodium and a fuel alloy containing 5 g of plutonium/cm^3 were in a tantalum capsule that was slowly rotated (one rotation every 10 min) for 96 hr at 600°C. Subsequent sectioning showed (1) complete wetting of the tantalum surface by sodium, (2) considerable sodium entrained throughout the fuel, and (3) no evidence of fuel entrapment in the sodium.

For determining the corrosion resistance of various materials to mercury, a Mercury Corrosion Loop Testing Program has been instituted at the Aerojet-General Corporation.[58] Materials to be tested in 10 forced-convection loops now under construction are: Haynes 25, 9 Cr–1 Mo alloy clad with type 316 stainless steel, AM 350 stainless steel, and niobium clad with type 316 stainless steel.

The presence of voids in the interior of an 18-8 stainless steel corroded by a fused 50-50 sodium chloride–potassium chloride melt in the presence of air was postulated by French workers to be caused by the selective removal of chromium by the corrosion reaction and diffusion of chromium to the surface, leaving behind the interior voids.[59]

IAEA Papers on Liquid-Metal Corrosion

The papers listed below on liquid-metal corrosion were presented at the IAEA Conference on the Corrosion of Reactor Materials held in Salzburg, June 4–9, 1962, and will be published in the proceedings of the conference:

1. *Corrosion Tests with Molten Plutonium Fuels.*[60] This paper gives information on the corrosion of tantalum and tantalum alloys by molten plutonium fuels used or to be used in LAMPRE or considered for fast plutonium reactors.

2. *The Relationship Between Oxygen Distribution and Corrosion in Some Refractory Metal-Lithium Systems.*[61] As the oxygen concentration was increased in niobium, tantalum, and vanadium, their corrosion resistance to lithium decreased. Additions of oxygen to zirconium did not affect its corrosion resistance to lithium.

3. *Resistance to Corrosion of Austenitic and Ferroperlitic Steels in a Stream of Liquid Sodium*[62] *at Temperatures of 600°C and 700°C.* The Russian authors of this paper describe the nature of the interaction of the steels with sodium during prolonged operation in a dynamic loop. The addition of 0.2% calcium to sodium significantly lowered the isothermal attack of austenitic steels by sodium.

4. *Liquid Metal Corrosion Mechanisms.*[63] This paper describes the kinetic and thermodynamic processes occurring during liquid-metal corrosion.

Twenty-two papers are included in the proceedings of a liquid-metal corrosion meeting held at Brookhaven National Laboratory and sponsored jointly by the National Aeronautics

and Space Administration (NASA) and AEC.[64] Subjects included are liquid-metal research, evaluation of materials in gaseous and liquid mercury, liquid-metal corrosion of loop materials, effects of potassium on refractory alloys, research program on sodium components, determination of oxygen in sodium, and sodium loop studies.

General Information

Procedures for the consumable-electrode arc melting of uranium have been reported.[65] Concentrations of a number of impurities in uranium were reduced by arc melting. Inclusions of impurities remaining in the arc-melted uranium were finely divided and evenly distributed.

A new book on the technology of fuel-element fabrication in the United States[66] contains 18 individually authored chapters. The metallurgy and properties of uranium and its alloys, of plutonium and its alloys, and of thorium and its alloys are discussed, as well as ceramic fuels, cladding materials, irradiation effects, engineering aspects of fabrication, inspection and testing, processing, and fuel-element economics.

A review[67] (in French) has also been issued on the extraction, physical properties, mechanical properties, physical metallurgy, and use of various nuclear materials, including uranium, thorium, and plutonium and their compounds.

The solubility and nature of bonding in solutions of an alkali metal in a fused halide of the same metal have been discussed.[68] In another investigation, thermodynamics of metal–fused chloride salt systems has been interpreted by diagrams in which the equilibrium potential of the system is plotted against the activity of the oxide ion in the chloride melt.[69] Electromotive force, polarographic, and chronopotentiometric measurements have been utilized in a study of bismuth–bismuth tribromide solutions.[70]

Other Nonaqueous Processes

Pyrochemical procedures, which are suited principally to oxide and carbide reactor fuels, generally utilize gases, molten salts, and liquid metals as reagents and process media. They resemble pyrometallurgical processes in the use of high-temperature reactions, a capability for handling short-cooled fuels, simplicity, and compactness. Both types of processes produce only moderate fission-product decontamination, and they are normally combined with remote fuel-fabrication techniques to form a complete reactor fuel cycle.

Oxide Fuel Processing

The salt-cycle process, under continuing development at Hanford, is an electrolytic procedure for the recovery of irradiated uranium dioxide–plutonium dioxide fuels.[71–73] The mixed oxide fuel is first dissolved in a molten chloride salt bath by sparging the mixture with chlorine or hydrogen chloride. A portion of the dissolved uranium, present as uranyl(VI) ion, is reduced cathodically to uranium dioxide. This material is essentially free of plutonium and is a by-product of the process. Further electrolysis then codeposits uranium and plutonium dioxides, yielding a product sufficiently enriched in plutonium for recycle to the reactor. In addition to the electrolytic process, alternative techniques such as selective precipitation of the oxides from molten-salt solution by chemical means are also under investigation.

The possibility of controlling the uranium-plutonium separation in the electrolytic deposition step through variations in cell voltage and current density has been demonstrated.[71] At a current density of 0.4 amp/cm^2 and an applied potential of 1.0 volt (vs. Ag/AgCl), deposition of uranium dioxide from 2.6 LiCl–KCl (2.6 : 1 mole ratio) at 600°C gave a plutonium decontamination factor of about 50. When the current density and the potential were halved, this value increased to an average of about 100.

The following reaction is involved in the dissolution and electrodeposition steps of the salt-cycle process:

$$UO_2(s) + Cl_2(g) = UO_2Cl_2(\text{solution})$$

Previously reported thermodynamic quantities for the reaction in NaCl-KCl at 993°K were derived from electromotive-force measurements.[74] More recently, similar measurements have been made in LiCl-NaCl at 943°K, with the results shown below:

Uranyl(VI) molal concentration	ΔF, cal/mole	ΔS, entropy units	ΔH, cal/mole
0.035	−25,300	3.2	−22,200
0.725	−18,600	9.8	− 9,300

In both solvent systems the thermodynamic values indicate a decreasing extent of complex formation by uranyl(VI) ion as its concentration is increased. Since the free-energy change is more positive in LiCl-NaCl than in NaCl-KCl, the activity coefficient of uranyl(VI) chloride is larger in LiCl-NaCl. This effect results from a lower chloride-ion activity in this solvent.[73]

Electrochemical studies have also been reported on the reduction of Pu(III) chloride in molten chloride media.[72] Voltametric measurements with a tungsten cathode in LiCl-KCl eutectic at 600°C show that the reduction occurs in two steps. Measured potentials for the second step indicate a two-electron change, leading to the overall reaction

$$\text{Pu(III)} + e^- \rightarrow \text{Pu(II)}$$

$$\text{Pu(II)} + 2\,e^- \rightarrow \text{Pu(0)}$$

Chronopotentiometric measurements were employed to determine diffusion coefficients for Pu(III) in 2.6 LiCl–NaCl, 7.7 LiCl–KCl, and LiCl–1.5 KCl at 600°C. In all three solvents the diffusion coefficients had essentially the same value, 3.0×10^{-5} cm^2/sec.

Further work has been reported on the precipitation of plutonium dioxide from molten chloride solutions by sparging with oxygen-chlorine mixtures.[71] Previous indications that the extent of plutonium dioxide precipitation is solubility-limited were confirmed, using starting concentrations of 0.1 and 1 wt.% plutonium in the salt. In both instances, about the same concentrations of soluble plutonium were found in the melt (between 0.012 and 0.03 wt.%) after the precipitation.

The relative efficiencies of the plutonium dioxide precipitation and uranium dioxide electrodeposition procedures in effecting separations from europium and promethium tracers were determined.[71] The precipitation reaction in LiCl–2.6 KCl at 575°C gave decontamination factors of 60 to 100 for europium and 600 for promethium. In the same type of melt at 600°C, the electrodeposition technique resulted in decontamination factors of 135 for europium and 1200 for promethium.

The effects of corrosion and fission-product impurities on the quality of the uranium dioxide produced in the salt-cycle process were examined in a series of electrodeposition runs.[73] The salt bath consisted of 40 wt.% LiCl and 60 wt.% KCl, and all the runs were 200 hr in duration. Iron, at a concentration of 1 wt.%, decreased the current efficiency and the crystal size of the deposited uranium dioxide. The product contained 100 ppm iron, had an oxygen-to-uranium ratio of 2.004, and was near the theoretical density. Additions of 1 wt.% nickel and 0.42 wt.% samarium had no adverse effects. With 0.2 wt.% aluminum in the melt, the product density was 88% of theoretical. Preliminary observations on melts contaminated with niobium and zirconium indicate that their presence rendered dissolution of the uranium oxides more difficult.

In another experiment the addition of 0.3 wt.% Fe(III) chloride to 2.6 LiCl–KCl at 575°C reduced the current efficiency from 70 to 60% in the electrodeposition process and lowered the decontamination factors for plutonium and europium by about 20%. The separation factor for iron (based on uranium) was 170. For the plutonium dioxide precipitation process, using the same melt, the presence of iron caused a factor of 2 reduction in the europium decontamination factor. The separation factor for the iron itself in the plutonium dioxide precipitation step was 4.3.

Electrolytic purification of contaminated alkali halide melts is receiving attention as a possible method of reducing salt waste volumes in the salt-cycle process.[72] With a molybdenum cathode and an open graphite anode, electrolysis at −2.0 volts (relative to Ag/AgCl) removed less than 5% of all the impurity ions. However, with a magnesia cell liner, a molten lead cathode, an open graphite anode, and a cell potential of 4.5 to 5.0 volts, high removals were achieved. Percentages of ions separated were: uranium, 99.99; iron, 97.5; plutonium, 98; and europium, 60.

Engineering and equipment development on the salt-cycle process has also continued at Hanford. Prototype equipment has been designed to investigate the handling of plutonium dioxide precipitates in molten salts.[73] Since the precipitate settles immediately upon formation, it

must be recovered from the bottom of the vessel. A freeze valve in the bottom of the vessel, together with a quartz frit filter, has been tested successfully to remove the molten salt from the settled precipitate. It appears, however, that breakage of the quartz tube used as the freeze valve may be a problem.

Some development of process instrumentation for the salt-cycle process has been reported.[71] A satisfactory liquid-level indicator with a range of 11 in. utilizes a quartz float buoying a rod. The location of the rod is detected by a position transducer. A microelectrode voltage control and power supply system has also been tested with satisfactory results.

ANL Report on Chlorination of Uranium Fission-Product Oxide Mixtures

An Argonne report has been issued on the chlorination of uranium–fission product oxide mixtures in molten halide media.[75] The mixed oxides were suspended in the molten salt, and the system was sparged with chlorine–carbon monoxide mixtures at 800°C. The salt was composed of alkali and alkaline-earth chlorides, with small amounts of fluoride (~5 mole %) present in some cases. The rate of oxide dissolution was dependent on the composition of the salt, and it was increased by additions of iron or zinc chlorides as catalysts. Under some conditions, greater than 99% removals of molybdenum, ruthenium, and zirconium were observed. This effect was attributed to the volatilization of chlorides of these elements.

Gaseous Low-Decontamination Process for UO_2

The development of a low-decontamination process for uranium dioxide fuels which utilizes only gaseous reagents has continued at Atomics International.[76–78] The irradiated uranium dioxide is alternately oxidized by air or dilute oxygen at 200 to 600°C and reduced by hydrogen at 600°C until the material becomes a fine powder suitable for remote refabrication by cold pressing and sintering. The cyclic oxidation-reduction procedure also serves to remove the oxide fuel from its stainless-steel cladding. Although some fission-product removal is achieved by this procedure (mainly cesium, ruthenium, tellurium, iodine, and the noble gases), the primary objective of the process is to facilitate reenrichment and refabrication of the fuel for recycle to the reactor.

To demonstrate the feasibility of the process, several complete cycles of decladding, processing, refabrication, loading of capsules, and reirradiation are being conducted with irradiated fuel. One complete cycle has been performed, using 100-g quantities of uranium dioxide fuel irradiated to 5700 and 15,000 Mwd/metric ton. The fuel was removed from the cladding and converted to a powder by the oxidation-reduction procedure, new pellets were formed by pressing and sintering at 1750°C for 11 hr, and then the pellets were loaded into welded capsules for further irradiation. During the sintering procedure, almost all the fission-product cesium was removed, but essentially no removal of plutonium and rare earths occurred.[77] The densities of the refabricated pellets were at least 90% of theoretical.[76] The capsules have not yet been inserted in the Materials Testing Reactor for further irradiation. At present their individual reactivities are being measured in the Reactivity Measurement Facility at the National Reactor Testing Station.[76]

Since most of the fission products are not removed from the fuel by this process, computer calculations were made to predict the effect of fission-product poisoning on reenrichment requirements for the processed fuel.[76] Assuming a burnup of 15,000 Mwd/metric ton, complete recycle of the plutonium generated during irradiation, and reenrichment by blending, the results show that about 10% greater U^{235} burnup is required if this process is used than is necessary for a process capable of complete fission-product removal. However, fuel-cycle cost studies indicate that increased cost of the additional U^{235} burnup is more than offset by lower cost of the simple fuel cycle. In a three-reactor complex, a net saving of 0.1 to 0.2 mill/kw-hr in comparison with conventional processes is considered to be a conservative estimate.[76]

Oxidation-Reduction of UO_2 Fuels

Research has also been conducted in Belgium on the oxidation-reduction of uranium dioxide fuels to increase the reactivity of the material for subsequent processing by chloride methods.[79] When the uranium dioxide is oxidized to U_3O_8, then reduced with hydrogen, water is formed as a by-product of the reaction

$$U_3O_8 + 2H_2 \rightarrow 3UO_2 + 2H_2O$$

The presence of water is undesirable in this case since it causes hydrolysis of the chlorides and corrosion of the equipment. The use of ammonia as a reducing agent has the same disadvantage. Methane has therefore been investigated as a possible reducing agent for U_3O_8 at temperatures of 500 to 550°C. Although this procedure does not avoid the formation of water completely, the quantity is reduced considerably. Water formation can be completely eliminated by using carbon monoxide as the reductant at temperatures between 450 and 500°C:

$$U_3O_8 + 2CO \rightarrow 3UO_2 + 2CO_2$$

However, the cost and toxicity of carbon monoxide are considered to outweigh the advantage. It was concluded that methane is the most promising reducing agent if the conditions are regulated to produce the minimum amount of water.

Carbide Fuel Processing

The development of three low-decontamination pyrochemical processes for uranium carbide reactor fuels has continued at Atomics International.[76–78] The major effort remains on a carbide-oxide-carbide cycle, in which the fuel is first oxidized by oxygen or carbon dioxide at about 400°C and then the resulting oxide is reconverted to uranium monocarbide by reaction with carbon at or above 1300°C. The product is arc melted to form a solid material suitable for reuse as a fuel. The second process involves a cycle in which the carbide is converted to uranium nitride by reaction with nitrogen, after which the reaction is reversed by heating the uranium nitride–carbon mixture under vacuum. A third process consists of electrolytic dissolution of the carbide in a molten chloride salt bath and deposition of metallic uranium on a molybdenum cathode. The uranium deposit is dissolved in mercury, then converted to the monocarbide with propane as the mercury is removed by distillation. The first two processes are primarily refabrication and reenrichment procedures. The electrolytic process, although more complex, is capable of significant fission-product removal.

Currently, a much greater proportion of the effort is devoted to the carbothermic reduction step of the carbide-oxide-carbide process.* The effect of fission-product elements on the reaction has been examined by arc-melting the product of a reaction of carbon with uranium dioxide that contained 5 wt.% fission-product oxides.[76] Metallographic examination of the arc-melted specimens showed a structure differing from that of pure uranium monocarbide in that very fine grains were found embedded in a uniform matrix. It is suspected that the fission-product elements serve as a carbon "sink," thereby preventing uranium dicarbide formation. Chemical analyses of the three samples before and after arc melting are given in the following table (theoretical for UC: 4.80 wt.%):

	Wt.% carbon	
Sample	As reacted	Arc melted
1	4.88, 4.94, 4.86	4.99, 4.99
2	5.41, 5.27, 5.36	5.43, 5.34, 5.34
3	5.60, 5.63, 5.62	5.67, 5.61

Unlike previous results obtained with uranium carbide produced from uranium dioxide only, no significant decrease in the carbon content occurred during arc melting of the three samples. Possibly some component of the fission-product oxide mixture catalyzes the oxygen-carbon reaction. Techniques are also being developed for carbothermic reduction experiments with irradiated uranium dioxide, the principal objective being to determine plutonium losses at high temperatures.[77]

The use of additional gaseous reagents to effect greater fission-product removals in the carbide-oxide-carbide cycle is under study.[78] In a typical experiment a pellet of uranium dioxide containing 10% fission-product oxides was first oxidized to U_3O_8 at 400°C and then treated with chlorine at 450°C and with hydrogen and hydrogen chloride at 650°C, after which the volatile materials were vacuum distilled at 900 to 1000°C. Individual fission-product removals were not reported; however, the weight loss corresponded to about 50% of the combined weights of rare earths, barium,

*A more general discussion of preparative methods for uranium carbide appears in Sec. V of this issue. The work referred to here applies specifically to the use of carbothermic reduction as an integral step of a remotely operated fuel cycle.

and strontium in the sample. No uranium was detected in the condensate.

Further results have been reported on scaleup of the carbothermic reduction step to the kilogram level.[76–78] The initial phase of the program is concerned with the uranium dioxide–carbon reaction in a vacuum induction furnace. Three experiments were conducted in which various types of uranium dioxide were dry-mixed with the stoichiometric amount of ball-milled graphite powder and agglomerated with binder and water to form balls $\frac{1}{8}$ to $\frac{3}{8}$ in. in diameter. After vacuum drying at 170°C and heating at 900 to 1000°C to remove the binder and reduce the higher uranium oxides, the specimens were heated at 1760°C under vacuum for 4 hr. Carbon and oxygen analyses of the product showed that efficient mixing of the reactants is essential in order to obtain a homogeneous product.[76,77]

In other experiments,[77] uranium dioxide prepared by oxidation-reduction of the carbide was mixed with carbon by wet ball milling and extruded through a 4-mesh screen. Part of the resulting material was reduced in tantalum, and part in graphite, in two 4-hr periods at 1650°C. Preliminary results show a lower carbon content for the product prepared in tantalum (5.09 wt.%, compared with 5.35 wt.% in graphite), suggesting that some carbon pickup occurs in the graphite crucible.

Some additional variables that affect the carbon content of the product were examined in experiments with 100-g mixtures of uranium dioxide and carbon.[78] Uranium dioxide samples used in study of the carbothermic reaction contain a slight excess of oxygen (oxygen-to-uranium ratio ~2.09). During the initial heating at 900 to 1000°C to remove the binder, this excess is removed. It is presently assumed that oxygen is removed from the system as carbon monoxide. The carbon-to-uranium ratio of the product will be affected by any different oxygen-removal mechanism, e.g., as carbon dioxide or oxygen. Another variable concerns the reaction of the uranium monocarbide product with atmospheric moisture after the uranium monocarbide is removed from the furnace. The changes in oxygen and carbon levels obtained upon reheating the material at 1650°C suggest that moisture had been present, since the changes are not compatible with the internal stoichiometry of the system.

Table III-8 EFFECT OF ARC MELTING ON SIX URANIUM MONOCARBIDE POWDERS PRODUCED BY THE NITRIDE PROCESS[77]

	1	2	3	4	5	6
Nitrogen prior to arc melting, wt.%	0.50	0.40	0.32	0.25	0.23	0.034
Arc-melting time, min	8	0.5	8	2	2	2
Loss during arc melting, %	3.1	1.0	3.0	3.9	2.0	2.9
Button weight, g	5.6	6.4	6.5	7.8	17.4	6.1
Nitrogen after arc melting, wt.%	0.078	0.24	0.065	0.091	0.11	0.029

In connection with the nitride process, a study has been conducted on the effect of nitrogen pressure on the particle size of the uranium nitride–carbon mixture obtained by reaction[76] at 750°C. Stepwise increases in the nitrogen pressure from 0.5 to 2.5 atm produced a progressively smaller particle-size product for a given reaction time. Experiments on the reconversion of uranium nitride–carbon mixtures to uranium monocarbide have shown the residual nitrogen content of the product to be independent of the particle size of the nitride.[83] The residual nitrogen content does appear, however, to be related to the carbon content of the product. The data given below were selected from results of the reconversion reaction conducted in vacuum[78] at 1700°C.

Nitrogen, wt.%	Carbon, wt.%
0.03	5.35
0.24	4.80
0.40	4.60
0.67	4.10

The results listed in Table III-8 were obtained by arc-melting several uranium monocarbide powders produced by the nitride process.[79] During the arc-melting operation, some nitro-

gen was removed, but little spattering took place. Four nitride processing cycles have been completed, using lightly irradiated uranium monocarbide samples.[78] Analytical results have not yet been reported.

Studies of the electrolytic process have involved the successive anodic dissolution of four uranium monocarbide pellets.[78] The molten-salt bath, composed of 10 wt.% uranium tetrafluoride added to lithium chloride–potassium chloride eutectic, was held at 450°C during electrolysis. The anode current efficiencies for the pellets were 127, 108, 82, and 72%. The initial anode efficiencies of greater than 100% indicated that some uranium monocarbide was dissolved by a reaction with the uranium tetrafluoride such as the following one:

$$UC + 3U^{4+} \rightarrow 4U^{3+} + C$$

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Section

IV

Reactor Fuel Processing

Waste Disposal

Design Criteria for Containers Used in Disposal at Sea

The AEC has published a report[1,2] prepared by the Southwest Research Institute, San Antonio, Tex., which deals with the design criteria for containers used in the sea disposal[3] of radioactive wastes. In establishing these criteria all available test results and information on the current techniques in sea-disposal operations were reviewed and considered. The report also includes discussions and recommendations on Portland-cement concrete as a construction material for radioactive waste packaging; on fabrication of reinforced-concrete structures for packaging radioactive wastes, waste placement and compaction, vents, and impact; and on radioactive waste containers in current use for sea-disposal operations.

Sea disposal of radioactive wastes requires that the final container have sufficient shielding for safe handling, sufficient weight to assure sinking, and sufficient structural integrity to assure containment of the packaged material to the desired depth. Also, the container must have a size and shape that will make it easy to handle. Concrete is the most feasible material for meeting all these requirements. Consequently the containers discussed in the AEC report are suitable for all wastes that are compatible with concrete encasement. Discussed are the existing standard containers, such as 5-, 30-, and 55-gal drums which utilize concrete for bulk and structural integrity, and larger concrete blocks cast to receive larger amounts of waste or wastes not suitable for drum packaging.

Treatment of Liquid Wastes by Ion Exchange and Foam Separation

Ion Exchange

At ORNL the development of a scavenging ion-exchange process for the routine removal of trace amounts of fission products from large volumes of process water has progressed through the laboratory, design, and pilot-plant phases.[3-5] In this process the contamination is removed in two steps: (1) the scavenging of a portion of the activity with sodium hydroxide and an iron coagulant, and (2) solution clarification and filtration and the sorption of Cs^{137} and Sr^{90} on a carboxylic-phenolic resin (Duolite CS-100). When 2000 resin-bed volumes, or 56,000 gal of waste water, have been passed through the bed, the feed flow is stopped, the fission products are eluted with 10 volumes of 0.5*M* nitric acid, and the resin is washed with water and regenerated with 0.1*M* sodium hydroxide.

Nine demonstration runs have been completed in the 10 gal/min pilot plant.[4,5] Some 50,000 to 90,000 gal of ORNL process waste water was treated per run, representing 1800 to 3000 resin-bed volumes. Run durations have varied from 71 to 146 hr of continuous operation. At the 2000-bed-volume level, the effluent contained less than 3% of current MPC_w (maximum permissible concentration in water) values for Sr^{90} and Cs^{137} for continuous occupational exposure. The decontamination factors ranged from about 2000 to 12,000 for strontium and from about 80 to 3500 for cesium.

The use of a "split-elution" procedure to decrease the volume of waste nitric acid eluant

was demonstrated. In this procedure, 5 bed volumes of 0.5*M* nitric acid eluant from the tail end of the previous elution is used as the initial removal solution. The first elution of contaminated salts and acid is sent to a regenerant-acid evaporator for processing and disposal. Then, to complete the elution, 5 bed volumes of fresh 0.5*M* nitric acid is passed through the resin column and sent to a recycle-acid storage tank. This second 5 volumes, containing almost no fission-product contamination, is held for a subsequent elution cycle.

Laboratory tests were undertaken to reduce the total hardness of the effluent from the clarifier unit used in the head-end or scavenging precipitation steps of this process.[3–5] The average total hardness of this stream has varied between 60 and 70 ppm (as calcium carbonate). Its decrease would substantially increase the on-stream life (80 to 100 hr) of the polishing filters. These filters not only remove colloidal calcium carbonate but also assist in the precipitation of carbonates from the clarifier effluent stream, decreasing the hardness from 70 ppm to the specified 10 ppm. A comparison of several treatment methods using ORNL tap water showed that an optimum treatment was obtained with 0.01*M* sodium hydroxide and 25 ppm calcium hydroxide (lime) at 24 to 26°C, producing a residual hardness of about 15 ppm without clarification. A test of this method in a continuous laboratory-scale clarifier, including the substitution of 5% sludge recirculation for the lime addition and adding 5 ppm ferric ion for floc formation, decreased the residual hardness to less than 10 ppm. Although this method was effective with tap water, it was not so successful on ORNL low-level-activity waste that contained trace amounts of complexing agents.

A conceptual design and cost estimate for a 750,000 gal/day scavenging ion-exchange treatment plant for treating the total ORNL process waste water stream indicated a capital cost of $511,000 and an estimated operating cost of 54 cents per 1000 gal, exclusive of amortization charges.[4] Amortization of the $511,000 investment over 20 years would add 9 cents per 1000 gal to the operating cost.

Decontamination of Purex Tank-Farm Condensate at Hanford

At Hanford, experiments were continued in the Micro Pilot Plant to develop an ion-exchange process for decontaminating Purex tank-farm condensate. In previously reported runs,[6] steam stripping followed by percolation through activated carbon beds has been used in Micro Pilot Plant experiments to remove organic matter from Purex tank-farm condensate prior to passing it through ion-exchange beds. In recent runs,[7] because of operating difficulties with the activated carbon beds, the ion-exchange units have been operated without any carbon pretreatment of the steam-stripped waste condensate.

To test this process modification, over 6000 column volumes of steam-stripped condensate were passed through a bed of Amberlite 200 (a sulfonated polystyrene cation-exchange resin). Except for ruthenium, the concentrations of the radioisotopes in the column effluent did not exceed their respective MPC_w's throughout the run. However, the pressure drop across the bed increased significantly (to about 5 psi per foot of bed depth at the end of the run) because of organic matter that caused the agglomeration of a 1-in. layer of resin at the top of the bed. Some organic matter was dispersed through the entire bed. Backwashing the bed with water was only partially effective in removing the organic material. The attainment of almost complete removal of the organic material required the mechanical breakup of the agglomerated mat that had settled to the bottom of the column during the backwashing operation; in addition a small amount of acetone was used to remove residual organic material adhering to the individual particles of resin. In a larger unit, backwashing with hot water together with mechanical or hydraulic agitation probably will clean the bed adequately prior to regeneration.

The Amberlite 200 ion-exchange resin bed was regenerated with nitric acid for a second run. For this run the steam-stripped condensate was acidified to *p*H 4 with nitric acid before being passed through the ion-exchange bed. Again more than 6000 column volumes was treated before the run was terminated. The decontamination performance of the bed was similar to that observed during the previous run, with slightly improved removal efficiency for strontium, cerium, and zirconium. Again ruthenium was not effectively removed. The addition of nitric acid to the feed, however, significantly improved the hydraulic characteristics of the bed, the pressure drop re-

maining essentially constant at less than 0.5 psi per foot of bed depth for the entire run.

Foam Separation

Fundamental and applied studies of the foam-separation process are continuing at ORNL (Refs. 3, 4, 8, 9, and 10).

A program to screen a representative sample of commercially available surfactants has been essentially completed.[4,9] Eight surfactants out of 107 tested were selected for more intensive study for application to specific problems, such as strontium and cesium removal from low-level-activity wastes. Of the eight surfactants, sodium dodecyl benzene sulfonate gave the highest strontium distribution coefficient, $\Gamma/x = 5 \times 10^{-2}$ cm, where Γ is the surface concentration of a component in moles per square centimeter and x is the bulk concentration of a component in moles per cubic centimeter. Various factors, such as sodium and calcium concentrations and pH, were found to change the efficiency of separating cesium or strontium from aqueous solutions.[4] Calcium interference was important in the foam decontamination of low-level-activity wastes from strontium, since the strontium distribution coefficient started to decrease when the calcium concentration exceeded about $10^{-4}M$, even with the better surfactants. Generally, the pH effect was not too important, since the strontium distribution coefficient remained high with one or more of the surfactants in the pH range of 2 to 12.

The decontamination factor, volume reduction, volumetric throughput rate, and distribution coefficient are some of the more important variables of countercurrent foam column operation.[4] Some of the relations between these parameters were established by a series of experiments in which foam density and linear foam velocity were varied. The height of a theoretical transfer unit for removal of strontium tracer in 2- or 6-in.-diameter columns was only 1 to 2 cm when the feed consisted of ORNL tap water (to simulate low-level-activity waste) that had been made basic to pH 11.8 by the addition of sodium hydroxide, which thereby reduced the calcium concentration from about 27 to 3.3 ppm. With such a low theoretical transfer-unit value, the foam height needed to obtain good decontamination was only about 1 ft.

Two potential applications of foam separation are the removal of cesium from evaporated neutralized Purex first-cycle waste (1WW) and of strontium and cesium from ORNL low-level-activity waste.[4,9] In the first application, copper ferrocyanide was added to a $6M$ sodium nitrate solution (to simulate Purex 1WW) to form the insoluble cesium copper ferrocyanide, which was removed, with gelatin as the surfactant, by a combination of foaming and flotation. In a nonoptimum batch experiment, 96% of the tracer cesium was recovered with a volume reduction greater than 300 and a cesium radioactivity distribution coefficient of 3×10^5 (counts per gram of solid/counts per milliliter of solution).

Studies of the decontamination of ORNL low-activity waste[4,8–10] were directed primarily toward removal of Sr^{90}. A proposed flow sheet is shown in Fig. IV-1. Further, since calcium interferes with strontium removal in foam decontamination, a laboratory-scale head-end precipitator-sludge column unit (with low-speed stirrer) was built to remove the calcium as calcium carbonate and magnesium as magnesium hydroxide by the addition of sodium hydroxide and/or sodium carbonate. To aid in the flocculation of the precipitate, ferric ion was also added. The sludge column acted not only as a partial filter but also as a zone for more complete precipitation of the calcium carbonate. The resulting low-hardness effluent from the precipitator-sludge column contained about 0.2 ppm suspended solids and is considered to be

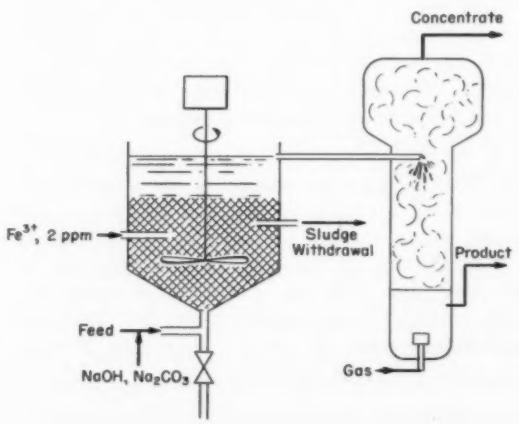

Fig. IV-1 Proposed flow sheet for ORNL low-activity-level waste decontamination.[4]

suitable for further strontium decontamination and volume reduction by foam separation.

In experiments with simulated ORNL low-level-activity waste, the dissolved calcium and magnesium were readily reduced to a total hardness of 1 to 2 ppm (as calcium carbonate), which corresponded to about 96% removal, by precipitation with $5 \times 10^{-3} M$ each of sodium hydroxide and sodium carbonate and by coagulation with 1 or 2 ppm ferric ion. Strontium was also removed by this treatment, the decontamination factors ranging from 20 to 200. Cesium removal was achieved by adding Grundite clay (0.5 lb/1000 gal). Decontamination factors that varied from 10 to 40 were obtained. A stirred sludge blanket height-to-diameter ratio of about 4 to 1 was used.

Strontium decontamination factors of up to 5000 were achieved in tests with a 6-in.-diameter countercurrent foam column using sodium dodecyl benzene sulfonate as the surfactant and a simulated effluent from the precipitator-sludge column. Volume reductions, which were not optimized, ranged from 25 to 1000. Further tests showed that the resulting foam condensate can be evaporated to dryness (volume reduction greater than 10^3) after the addition of a few parts per million of silicone antifoaming agent.

Conversion of High-Level-Activity Wastes to Solids

In-Tank Solidification

Plans for the treatment of Hanford production-plant wastes include evaporation, concentration, and solidification of certain of these wastes in large underground storage tanks.[3,7] The proposed method will employ electrically heated hot-gas sparging in a submerged gas-lift type circulator. Wastes will be continuously added to the concentration tank, and thus a nearly constant liquid level will be maintained as water is evaporated at temperatures below the normal boiling point. The addition of waste will continue until the tank is full or the hot-gas sparger ceases to circulate the remaining liquid. It is expected that the solution remaining at the end of sparging will solidify on cooling. Analytical and small-scale experimental studies of the in-tank solidification process are under way. The circulation pattern and solids-formation pattern within a tank are being investigated in small-scale model tanks. The behavior of the circulator under various process operating conditions will also be studied.

The circulation pattern experiments are being done in a shallow tank, 10 ft in diameter by 3 ft in depth. It is intended to determine whether the circulation pattern is dependent only on the volume of liquid circulated and is independent of viscosity and other liquid properties. This would then simplify the task of operating a representative model because it would no longer be necessary to maintain the same Reynolds number in the model as in the production-scale tank. A mathematical study of the circulation pattern within a large tank was also started.

The solids-formation pattern study is being done in an open-top tank, 4 ft in diameter by 15 in. in depth, equipped with a $1\frac{1}{2}$-in.-diameter centrally located simulated circulator. Concentrating liquor is withdrawn from the base of the circulator and is electrically heated and then discharged at approximately 4.5 gal/min at the top of the circulator. The flow pattern external to the circulator simulates the flow pattern expected in the full-scale system.

Two runs in this tank have successfully demonstrated that in-tank solidification can be achieved. In both runs, coating waste from the decladding (aluminum) of reject fuel elements was used for feed material. In the first run, which lasted 90 hr, additional sodium nitrite was added to the feed to simulate actual production plant coating waste. The contents of the model tank solidified completely on cooling. Maximum temperature obtained during the run was 132°C. The volume reduction factor was about 5, and the solids showed no sign of deliquescence.

In the second run no additional sodium nitrite was added to the coating waste. Solidification and plugging of the heated recirculation loop occurred after 174 hr of operation. The terminal temperature was 125°C. At the time of shutdown, 6 in. of solids had accumulated within a total freeboard depth of 12 in. On cooling, further solidification took place with crystal growths rising well above the top of the tank. Extensive cracking of the solid cake occurred, and remaining fluid drained through the cracks to the bottom of the tank. Preliminary analysis of the feed indicated that excessive sodium

hydroxide concentration (4.7*M*) probably prevented complete solidification due to deliquescence.

Pot Calcination

ORNL is continuing its development of a process for converting high-level-activity wastes to solids by high-temperature pot calcination.[6] In this process, wastes are evaporated to dryness, and the residual solids are calcined in a cylindrical stainless-steel pot which, when sealed, also serves as the final storage container. The process is not only suitable for handling a variety of waste types but also offers the possibility of fixing the fission products in glassy materials of very low solubility. A pilot plant to demonstrate this process with actual high-level-activity wastes is being designed. Its location has been changed from ICPP to Hanford.[3,4] For a summary of ORNL laboratory- and engineering-scale pot-calcination studies for the period July 1961 to June 1962, the reader is referred to the Annual Progress Report for the Chemical Technology Division.[4] This work has been covered in a previous Review.[6]

In laboratory-scale studies[4] of fixation in glassy solids, simulated TBP-25, Purex, and Darex-waste oxides were incorporated into glassy solids by fluxing with phosphite and one or more other fluxing agents (borax, silica, sodium hydroxide, aluminum phosphate, and the oxides of lead, calcium, and magnesium).

The products formed from simulated TBP-25 waste appeared to be true glasses over a fairly wide range of compositions. Initial softening points varied from about 825 to 1000°C. After melting the glasses, softening points were as much as 200 to 300°C lower than their initial values. The waste oxides in the glass varied from about 26 to 35 wt.%. Densities of the glasses ranged from 2.4 to 2.8 g/cm^3, and volume reduction factors (from the concentrated waste solution) varied from 7.2 to 9.3. X-ray analyses showed amorphous patterns. The semiengineering-scale fixation of TBP-25 waste in a glass incorporating 26 wt.% simulated waste oxides was accompanied by volatilization of 12.5% of the ruthenium, with physical entrainment of 0.02% or less. Sodium hypophosphite and lead oxide had been added to the waste to prevent ruthenium volatility and to serve as glass formers and modifiers. The thermal conductivity of this glass increased from 1.05 at 300°F to 1.60 Btu/(hr)(ft)(°F) at 1050°F. The thermal conductivity of the glass, at the softening point, about 1100°F (about 600°C), measured 1.51 at 1145°F and 1.40 at 1150°F.

The glassy solids from the fixation of Purex-waste oxides were often microcrystalline, particularly when prepared in a large batch that cooled slowly. Satisfactory products incorporated 36 to 45 wt.% waste oxides and had densities of 2.6 to 2.8 g/cm^3, volumes representing 4.8 to 6.9 gal of glass per ton of uranium, and initial softening points of 840 to 975°C.* The addition of extra acid anions (such as borate, phosphate, or phosphite) necessary for glass formation necessitated careful control of temperature during the calcination-fixation process in order to avoid loss of sulfur trioxide (SO_3) by volatilization. Thermogravimetric analysis of a typical Purex "glass" indicated that SO_3 was volatilized slowly, if at all, below 900°C and rapidly above 1000°C. It appears feasible to use temperatures high enough to produce glassy products and yet low enough to avoid substantial loss of SO_3.

Glassy products containing 13 to 22 wt.% Darex-waste solids were prepared. Densities varied from 2.7 to 3.8 g/cm^3, volume reductions varied from 2.9 to 6.6, and initial softening points varied from 850 to 900°C. The production of true glasses incorporating greater than 20 wt.% Darex-waste oxides is difficult because of the exceptionally high content of iron, nickel, and chromium, which do not form glasses.

Data from laboratory ruthenium volatility studies indicate that ruthenium volatility is minimized during the evaporation-calcination cycle by (1) low acid concentration, (2) distillation under reduced pressure, and (3) the presence of phosphite in the still pot.[4,5,11]

Holmes at ORNL has shown in a mathematical study[5,12] that a program will be required for controlling the wall temperature of a pot calciner during calcination in order to prevent an excessive temperature rise from internal heat generation while assuring complete calcination

*Although the initial softening point of the glass as formed by evaporation, calcination, and melting was about 950°C, the softening point of the glass after being formed was about 600°C.

of the cake at 1650°F. A linear approximation to a pot wall temperature program indicates that this can be accomplished by holding the wall temperature at 1650°F for 0.8 to 1.0 hr and then cooling the wall at rates dependent upon the cake internal heat-generation rate and average thermal conductivity. A similar study indicates that, if it is necessary to reheat the cake for complete calcination, the wall heating time must be limited to prevent excessive temperature rise in the cake. Reheating times are also dependent upon the cake internal heat generation and thermal conductivity.

Fluid-Bed Calcination

The ICPP is continuing its development and demonstration of the fluidized-bed calcination process for high-level-activity aluminum nitrate wastes.[6,13] The Demonstrational Waste Calcining Facility (DWCF) has been built to demonstrate this process with high-level-activity wastes. Testing of the DWCF with nonradioactive feeds is under way.

In pilot-plant studies, feed rates from 5 to 150 liters per hour per air-atomizing nozzle have been used with no perceptible tendency toward caking. Measured heat-transfer coefficients ranged from 40 to 110 Btu/(hr)(sq ft)(°F), depending on bed particle size and fluidized-bed density.

Particle size has been controlled by varying the atomizing air rate, which is the major factor governing particle attrition. Quantitatively, this effect is very dependent on the crystalline form of alumina produced. Various operating factors make significant differences in the rate of conversion of amorphous alumina calcine to the alpha (or, in isolated cases, to the gamma or iota) crystalline form. Particle attrition increases with alpha-alumina content. Hence average bed particle size decreases and particle elutriation rate increases with increasing alpha content. High-alpha-content beds are more dense and contain less nitrate. Both of these features are desirable. Sodium is a necessary feed ingredient for alpha-alumina formation; however, its effect can be overcome by addition of boric acid to the feed.

Intraparticle porosity varies from 5 to 60% and is a direct function of bed temperature (from 250 to 550°C) and feed concentration (from 0.8*M* to 2.0*M* aluminum) but is not a significant function of any other variable. Superficial fluidizing velocities from 0.5 to 2.5 ft/sec have been used; however, best results have been obtained with velocities under 1.0 ft/sec.

Studies have been made with and without condensing the off-gas stream and with near-total recycle of noncondensable off-gas for fluidization. The latter method of operation shows promise for minimizing atmospheric contamination.

The DWCF was operated continuously for 250 hr. Good mechanical operability of process equipment and close control of process conditions were demonstrated. Escape of solids past the calciner primary cyclone into the liquid scrubbing system continued to be a principal area of concern. Although solids carryover past the primary cyclone was reduced in this run to 20 lb/hr from the 32 lb/hr previously experienced, this carryover, which was approximately one-third of the theoretical product rate, is considered excessive.

Pilot-plant calciner runs were made to obtain information on the effect of feed and atomizing nozzle air rates on carryover of solids from the fluidized bed. Data from these runs indicated that solids elutriation rate from the calciner bed was dependent on the liquid feed and the nozzle air rate. The carryover increased rapidly as the alpha content of the bed increased; however the rate of solids carryover from the cyclone was constant, whether the bed was predominantly alpha or amorphous alumina. The solids carried over from the calciner bed appeared to be largely freshly formed alumina originating from the outer layer of the bed particles.

Final Storage of Calcined Solids in Salt Mines

ORNL is continuing its study of the use of salt mines for the storage of packaged calcined wastes.[6] A conceptual design was developed to determine which variables are important contributors to the cost of storage of solids in salt mines, and some preliminary cost figures were estimated.[4,5]

In the conceptual design the waste-container shipping cask is removed from a railcar and carried into a hot cell (Fig. IV-2) that encloses the top of the waste shaft. The con-

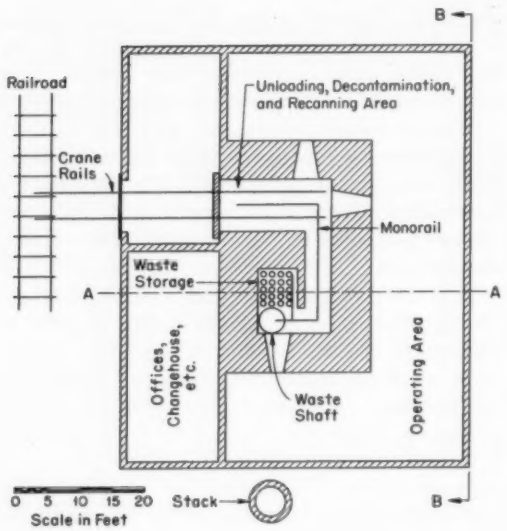

Fig. IV-2 Plan view of waste-shaft surface facility.[5]

tainers are removed from the shipping cask and placed in a storage area. The containers are removed from the storage area and lowered down the waste shaft into a motorized carrier at the working level of the mine (Fig. IV-3). The carrier moves out to the disposal area, lowers the container into a hole in the floor, and backfills the hole with fine crushed salt. Concurrently, salt is mined in another corridor. A 1-mile-square area is assumed to be served by a single waste shaft. The operations will be conducted on one quadrant of the mine at a time, completely isolating the salt mining from the disposal operations. Disposal-operations personnel and equipment will use the mining shaft for entering and leaving.

Ventilating air will come down a compartment in the mining shaft, with a portion being split off into the disposal tunnel. The disposal-tunnel air will travel completely around the quadrant and exit up the waste shaft. The air will be drawn from the shaft, through the hot cell, through an absolute filter, and up a 200-ft-high stack. Ventilating air will never pass a filled storage area before it reaches the current working area because disposal operations will start at the most remote point and work back toward the shaft. The criteria for isolation and ventilation require that a double tunnel be driven completely around the quadrant and that the rooms on the outside of the peripheral tunnel be excavated before disposal operations start.

Cost figures were calculated for the disposal of calcined Purex and Thorex wastes at a depth of 1000 ft for two conditions of disposal-room stability, one with very small structural flow and 2.5% dimensional closure due to thermal flow, and one with considerable structural flow and 100% dimensional closure due to thermal flow. The dimensional changes of the rooms due to thermal expansion and plastic flow must be considered because of the elevated temperatures arising from the fission-product heat from the calcined solids. The problem of predicting the thermal closure of a cavity in salt has not been completely resolved, but an approximate calculation was made for purposes of this study.

For the cost calculations, waste ages at burial of 1, 3, 10, and 30 years were assumed. The costs of developing peripheral tunnels and storage space were based on an assumed cost of $2 per ton for salt removal. Shafts and life-of-shaft items were amortized over the time required to fill the entire square mile (8.5 years for one year's decay with 2.5% closure to 89 years for 30 years' decay with 100% closure). Other items were amortized over 10, 20, or 50 years.

Total costs ranged from 6×10^{-3} mills/kw(e)-hr for 100% room closure with 30-year-

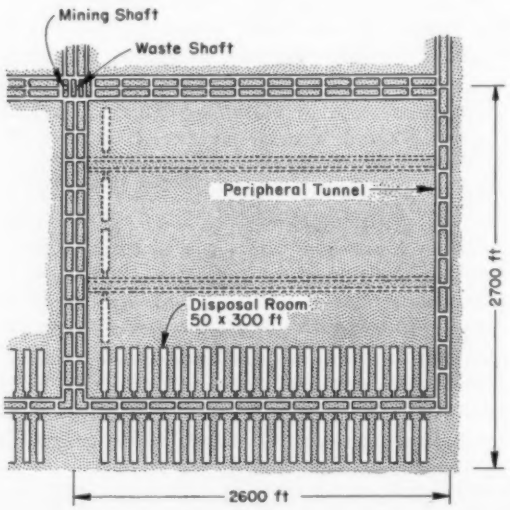

Fig. IV-3 Plan view of one quadrant of 1-mile-square disposal area.[5]

cooled wastes to 30×10^{-3} mills/kw(e)-hr for 1-year cooling and 2.5% closure. Sixty to 85% of the costs were for salt removal, indicating that it is important to have the best possible estimates of this operation for the more detailed final study.

Shipping costs for calcined Purex and Thorex wastes were calculated, assuming cylindrical carriers of iron, lead, or uranium, with an inside diameter of 5 ft.[4,5,14] The vessels containing the calcined solids were the 6-, 12-, and 24-in.-diameter cylinders used for pot calcination. Carriers would contain thirty-six 6-in.-diameter vessels, nine 12-in.-diameter vessels, or four 24-in.-diameter vessels. The carriers were air filled and had no mechanical cooling equipment.

Weights and costs for carriers at minimum waste ages for shipping of wastes were about 100 tons and $50,000 for iron carriers, 80 tons and $120,000 for lead carriers, and 65 tons and $650,000 for uranium carriers. The shipping costs were calculated for round-trip distances of 1000, 2000, and 3000 miles. Shipping costs were lowest in all cases for lead carriers, but in some cases the use of lead carriers required higher minimum waste ages. At 1000 miles the use of iron carriers costs less than that of uranium carriers, but at 3000 miles the cost of uranium carriers is less than that of iron carriers and approaches that of lead carriers. Costs for lead carriers range from 5.5×10^{-4} mills/kw(e)-hr for acidic Purex waste at 30 years of age in four 24-in.-diameter cylinders per carrier at 1000 miles to 1.6×10^{-2} mills/kw(e)-hr for acidic Thorex at 0.33 year in four 6-in.-diameter cylinders or one 12-in.-diameter cylinder. Costs for 3000-mile round-trip shipments were higher by factors of 2.0 to 2.4.

The effect of fission-product removal on the cost of high-level-activity-waste management was investigated through interim liquid storage, pot calcination, and shipment to salt mines for permanent disposal.[15] The study indicated that fission-product removal would not significantly decrease waste management costs. The costs of interim liquid storage were decreased about 30% over those of untreated wastes because of decreases in cooling-system requirements, but pot-calcination costs were unaffected, except that all calcinations could be performed immediately in the least expensive 24-in.-diameter pots. Minimum total costs (less the cost for disposal in salt) were about 0.141 mill/kw(e)-hr for 99% removal and 0.147 mill/kw(e)-hr for 90% removal, as compared with 0.147 mill/kw(e)-hr for acidic Purex wastes from which fission products had not been removed.

Extraction of Fission Products

As a part of its Waste Management Program, Hanford is developing processes for the extraction of long-lived heat-producing fission products from formaldehyde-treated Purex acid wastes (FTW).[6,7] Ion exchange and solvent-extraction processes are being studied.

In a current flow sheet[7] for the extraction, gross purification, and recovery of cesium from Purex FTW, the clarified FTW is passed through a bed of clinoptilolite. Cesium and some sodium are adsorbed on the mineral, whereas the other cations are only slightly adsorbed. Ninety-five percent of the sodium and only 0.1 to 0.5% of the cesium are eluted with 12 column volumes of 0.25*M* nitric acid. Following a water wash, the hydrogen ions are removed with 3 column volumes of 1*M* ammonium hydroxide. Less than 0.2% of the cesium is lost to these washes. Ninety-eight percent of the cesium is subsequently eluted with 7 column volumes of 2*M* ammonium carbonate at 55°C. The ammonium carbonate is then volatilized from the eluate, leaving a solution containing essentially pure cesium carbonate. The cesium can then be loaded on a high-capacity inorganic ion exchanger for storage. Cesium stored in this way is amenable to future recovery. Loadings equivalent to 20 to 40 wt.% cesium are possible. In a test of this flow sheet using a simulated Purex FTW, the load-wash-elute cycle was repeated eight times. The acid in the waste appears to attack the clinoptilolite very slowly, releasing about 100 ppm aluminum to the effluent and a small amount of silica to the eluate stream. The volume to cesium breakthrough decreased by about 2% per cycle.

The separation of cesium from mixed fission products was investigated using the same process as above, except that a 1*M* nitric acid eluant was used for removing sodium from the clinoptilolite column. A lower acid concentration, 0.25*M* to 0.50*M*, is now considered opti-

mum for this step. A simulated FTW containing added mixed fission-product activity from actual Purex 1WW was used for feed. Cerium, strontium, and ruthenium reached 50% breakthrough in about 1 column volume. Cesium reached 50% breakthrough in 87 column volumes. The niobium breakthrough did not exceed 5%. Zirconium tracer was absent in the feed and was assumed to have precipitated or plated out on the surface of the feed container. The decontamination factors for cesium from several fission products of interest were as follows: cerium, greater than 9.0×10^4; strontium, 2.1×10^3; ruthenium, greater than 1.4×10^5; and, niobium, 7.0. Solids, believed to be silica, were present in the ammonium carbonate eluate from the cesium elution step, but they were less than 1% of the eluate volume. About 90% of the cesium present in these solids could be removed by washing with ammonium carbonate.

Experimental data were obtained which indicated that the gassing of ammonium carbonate solutions in a column of clinoptilolite can be minimized by maintaining the temperature at or below 55°C and by addition of ammonia to the ammonium carbonate solution.[7]

The elution of cesium or strontium from high-capacity inorganic exchangers that were heated to 600°C for 24 hr after loading was also investigated. From the elution standpoint the best exchangers in this test for cesium storage were clinoptilolite, Zeolon, and Linde 13X. From 97 to 99% of the cesium can be eluted from clinoptilolite and Zeolon by using ammonium nitrate and from Linde 13X by using nitric acid. Strontium was tested with only one exchanger, Linde 4A molecular sieves, 99% being eluted with nitric acid. The amounts of cesium or strontium vaporized during heating (static condition) were very small and amounted to from zero to less than 0.1%.

A solvent-extraction flow sheet, which Hanford is studying for the removal and separation of strontium and rare earths (particularly cerium) from Purex FTW, employs di-2-ethylhexyl phosphoric acid (D2EHPA) diluted with Soltrol containing tributyl phosphate (TBP) as the extractant.[7] In the current flow sheet, citric acid is used in the feed to the extraction column as a buffering and complexing agent.

Mixer-settler runs of the extraction cycle have demonstrated that, with seven extraction and five scrub stages, strontium extraction was greater than 99% and cerium and promethium extraction was greater than 90%. Decontamination from cesium, zirconium-niobium, ruthenium, chromium, nickel, sodium, and uranium was excellent. Decontamination from iron was adequate but was less than the decontamination obtained when hydroxyethylene diamine triacetic acid (HEDTA) was used as a complexing agent. Strontium is separated from rare earths in the second or partitioning column with dilute nitric acid as the partitioning agent. In runs with a miniature mixer-settler simulating the second column, the organic extractant from the first-cycle extraction runs was used as feed. After seven stages, strontium loss was 0.3%, and the cerium decontamination factor was about 500. The rare earths are stripped from the organic with 2*M* nitric acid in a third column.

Strontium and Rare Earths at ORNL

At ORNL a three-cycle solvent-extraction flow sheet[3,4] for recovering and separating strontium and mixed rare earths with D2EHPA was demonstrated successfully in continuous miniature mixer-settler equipment using actual Purex 1WW solution from Hanford. This process[4] was further developed and modified at Hanford to recover megacurie quantities of Sr^{90}.

In the first cycle of the ORNL process, the strontium and rare earths are coextracted. Sodium tartrate was added to the feed to complex the iron and other cations, and sodium hydroxide was added to *p*H 6. The strontium and rare earths were coextracted with D2EHPA-TBP-Amsco 125-82 and then costripped with nitric acid. The overall first-cycle recovery for strontium and for rare earths was 99.7 and 80%, respectively. Overall decontamination factors for strontium in the first cycle were 45 from cesium, 170 from ruthenium, 3000 from zirconium-niobium, 2000 from iron, 2000 from uranium, and 30 from plutonium.

In the second cycle, rare earths are selectively extracted. The nitric acid strip product from the first cycle was used for feed after adding sodium tartrate and sodium hydroxide to *p*H 2. The solvent-extraction stream was scrubbed with sodium nitrate and sodium tartrate to improve the separation of the rare earths from strontium and was stripped of its rare-earth content with nitric acid. Recovery of rare earths in this cycle was greater than 99%; the rare-earth product solution contained less than 1% of the strontium. Decontamination

factors for the rare earths were about 80 from strontium, 120 from cesium, 100 from ruthenium, 45 from zirconium-niobium, and 170 from sodium.

In the third cycle the strontium is concentrated and is separated from sodium. The feed, raffinate from the second cycle, was adjusted to *p*H 6 with sodium hydroxide. Recovery of strontium was 99%, with decontamination factors of 90 from cesium, 90 from ruthenium, and 170 from zirconium-niobium. The strontium product solution contained about 1.2 g of strontium, 1.4 g of nickel, and 20 g of sodium per liter. Subsequent batch tests indicated that a nickel-free strontium product could be obtained by adding a small amount of ethylene diamine tetraacetic acid to the third-cycle feed to prevent extraction of nickel. Because of pump limitations, the organic-to-aqueous flow ratios used in the second- and third-cycle stripping were 2 to 1 rather than 5 to 1 as specified for the flow sheet. The rare-earth and strontium product solutions were therefore correspondingly more dilute.

Batch studies to improve this flow sheet indicated that (1) the strontium-to-sodium separation factor for the third cycle can be increased by a factor of 10 to 100 over that obtained in the continuous demonstration run described above and that (2) the flow sheet organic-to-aqueous strip ratio for the third cycle can be increased by an order of magnitude to provide a much more concentrated strontium product solution.

In preliminary testing at ORNL, amine extraction was shown capable of removing nitric acid, iron sulfate, and certain fission products from Purex 1WW.[4] This treatment would greatly decrease the amounts of sodium hydroxide and sodium tartrate needed to adjust the Purex 1WW to conditions suitable for strontium and cesium extraction, and, the adjusted feed, owing to its lower salt content, would be more amenable to treatment by these processes. Data from laboratory tests suggest that a single extraction contact would remove greater than 95% of the nitric acid and iron, greater than 98% of the zirconium-niobium, and the bulk of the ruthenium and rare earths from Purex 1WW without removing important amounts of strontium or cesium from the solution. Extraction of rare earths can be prevented, if desired, by accepting less efficient removal of iron.

ORNL is examining the use of substituted phenols[4] at a *p*H of about 12 for recovering cesium from Purex wastes and tank-farm supernatants. Of the compounds examined, excellent results were obtained with *p*-dodecylphenol (PDP), *o*-phenylphenol (OPP), and 4-chloro-2-phenylphenol. These compounds have adequate extraction power for cesium recovery, give good decontamination from fission products and other components of the waste, and are easily stripped with nitric acid. Of the diluents used with the phenols, best results were obtained with substituted benzenes, e.g., xylene and diisopropyl benzene. Cesium extraction coefficients with nitrobenzene diluent were higher than with other substituted benzenes, but phase separation was relatively poor.

A process flow sheet (Fig. IV-4) to recover cesium from Purex wastes was demonstrated successfully in batch countercurrent tests using 4-chloro-2-phenylphenol in diisopropyl benzene for the extractant and simulated Purex 1WW adjusted to *p*H 12.6 for the feed. Removal of about 99% of the cesium from the feed was accomplished in six extraction stages. Essentially all the cesium (99.8%) was stripped from the extractant stream by a single batch contact with nitric acid. The overall cesium-to-sodium decontamination factor was about 6000. Under the same flow-sheet conditions,

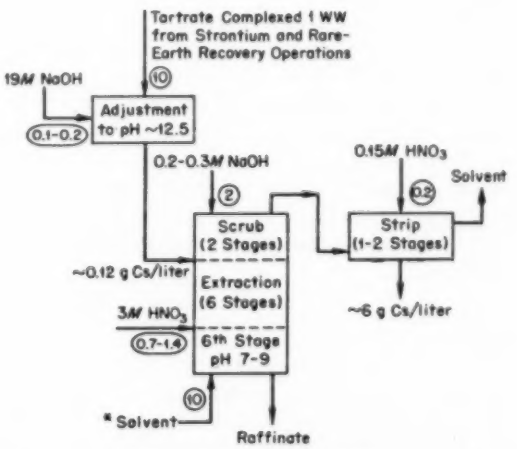

Fig. IV-4 Recovery of cesium from Purex waste by extraction with substituted phenols.[4] Circled numbers show relative volume flows.

but with feed adjusted to 0.8*M* instead of 0.6*M* excess sodium hydroxide, results were approximately equivalent with OPP in diisopropyl benzene.

Orr has reported that the ORNL Isotopes Division has modified a previously used ion-exchange Pm^{147} recovery procedure[16,17] so that it is capable of producing a high-purity (99%) Pm^{147} with little or no Am^{241} as the contaminant.[18] An americium decontamination factor of 2.7×10^9 was achieved with this modified procedure. This is the highest decontamination factor yet achieved for this separation. The separation of the americium from the promethium was accomplished by using Dowex 50W-X4 cation resin (hydrogen form, 80 mesh) and eluting with 0.5% diethylene triamine pentaacetic acid (DTPA) solutions at *p*H 5.5 at a temperature of 70 to 80°C.

Results obtained from tests with DTPA have shown that it changed the usual order of rare-earth elution. The americium was separated from promethium by the change in the order of elution of americium. In a system using 0.2*M* citric acid as eluant, the americium was eluted together with the promethium. In the DTPA system, americium was eluted together with europium.

This process was demonstrated by separating, in two runs, some 2 g of promethium oxide (Pm_2O_3) from 9 g of fission-produced rare-earth and americium oxides.[18] Promethium, computed as the element, was present to the extent of about 23.5 wt.% in the starting mixture and was increased to 98 wt.% in the first run and to 99 wt.% in the second, with yields of about 58 wt.% and 62 wt.%, respectively. The starting mixture contained about 6 wt.% americium oxide (Am_2O_3) and about 72 wt.% combined oxides of samarium and neodymium (Sm_2O_3, Nd_2O_3).

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Section

V

Reactor Fuel Processing

Production of Uranium, Thorium, Plutonium, and Their Compounds

Recovery of Uranium from Ores

At the Consolidated Denison Mines, Ltd., plant at Blind River, Ontario, Canada, uranium is leached from the ore by sulfuric acid.[1] The solubility of the uranium minerals in sulfuric acid solution is not high, and although good leach extractions are achieved in practice, they are obtained at the expense of elevated temperature, a strong acid solution, long leaching period, and the use of relatively large quantities of chemical oxidant. The leaching solution is generally maintained at 57°C. Partial recirculation of the leach discharge solution is employed to reduce the acid consumption. This recycle also results in a buildup of ferrous and ferric ions in the solution, thereby lowering the sodium chlorate oxidant requirement. The average sodium chlorate usage is 2.7 lb/ton of milled ore. The uranium leach solution is clarified by a sequence of operations before being fed to a series of ion-exchange columns.

The clarified leach solution is concentrated by the ion-exchange process from 0.9 g of U_3O_8 per liter to 19.0 g of U_3O_8 per liter. The Denison plant uses a moving-bed process, so called because the ion-exchange resin is hydraulically transferred from the adsorption columns to the backwash column and later to the elution columns. The exchange medium is Rohm and Haas Amberlite IRA-400 resin.

The ion-exchange plant comprises two identical units, each consisting of six 8-ft-diameter

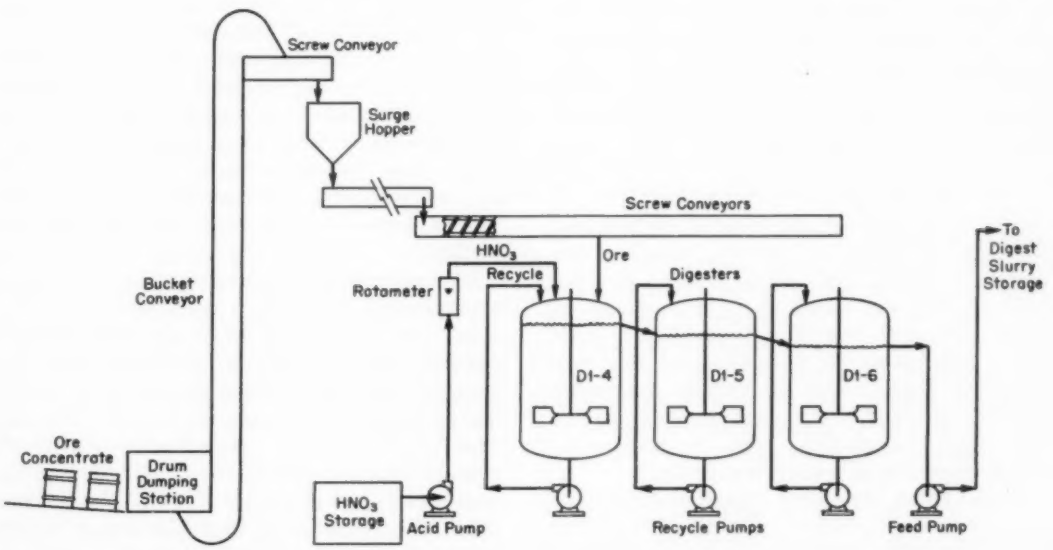

Fig. V-1 Plant test continuous digestion system.[2]

by 12-ft-high adsorption columns, one 8-ft-diameter by 16-ft-high backwash column, and three 8-ft-diameter by 12-ft-high elution columns. The six adsorption columns are arranged in two parallel circuits, each with three columns in series. These two units process an average of 9500 tons of feed solution per day.

Uranium in the clarified leach solution is adsorbed as the $UO_2(SO_4)_3^{4-}$ ion. After a column of resin has reached saturation, the resin is hydraulically transferred with clarified leach solution to a backwash column and then to the elution stage. Backwash consists primarily of flushing clarified leach solution upward through the loaded resin for removal of any slimes that may have passed the clarification stages. Clarified leach solution is used for both resin movement and backwash because it avoids the precipitation of hydroxides by hydrolysis, which would be likely to occur if water were used. After transfer of the loaded resin from a backwash column to the elution columns, the uranium is removed from the resin in a solution 0.3*N* in nitric acid and 0.7*N* in magnesium nitrate.

The recovery of uranium from the nitrate eluate is accomplished in a series of precipitation steps. The first step of the precipitation involves the removal of sulfate by the addition of a lime slurry to the solution to precipitate the sulfate as gypsum. Precipitation and recovery of uranium is subsequently accomplished by adding sufficient magnesia slurry to the filtrate to achieve a *p*H of 5. The magnesium diuranate is recovered by filtration and then dried to a 2% moisture content.

Study of Batch Vs. Continuous Operation at National Lead

Study of the process employed at the National Lead Co. of Ohio for refining uranium ore concentrates indicated that the overall process could be improved substantially if the digestion procedures were converted from batch to continuous operation.[2] It was expected that this transition would result in reduced materials handling and manpower requirements. At the same time, production could be increased, thereby reducing unit operating costs.

Three batch digesters were modified and converted to a continuous digestion system for three tests (Fig. V-1). The equipment selected allowed a 3-hr slurry retention time at the maximum production rates. A blend of Denison and South African concentrates with uranyl ammonium phosphate cake was used as feed material. Nitric acid concentration in the dissolver solution ranged from 9.6*N* to 11.2*N*. Digest feed slurries that were produced from standard uranium concentrates were satisfactory in all respects for subsequent solvent-extraction recovery of uranium containing 560 ± 50 g of uranium per liter and 3.2 ± 0.4*N* nitric acid. Digestion efficiencies were greater than 99.93%. On the basis of this work, the refinery was converted to a continuous digestion process.

Workers at National Lead Co. of Ohio[3] have prepared a correlation of the nitric acid consumption with the uranium content of ore concentrates in order to assist in establishing process control in blending procedures.

Production of Uranium Dioxide

Conversion of Uranium Hexafluoride to Uranium Dioxide

A fluid-bed process for the preparation of ceramic-grade uranium dioxide from uranium hexafluoride is being studied at ANL[4–7] for application to the production of nuclear fuel. Two different process schemes have been evaluated. The first of these is a two-step process in which uranium hexafluoride reacts with steam to form uranyl fluoride that is subsequently reduced to uranium dioxide by a steam-hydrogen mixture. The other scheme, which is a direct conversion to uranium dioxide in a single step, has been demonstrated in a fluid-bed reactor using the high-temperature reaction of uranium hexafluoride with hydrogen and steam.

The first step in the conversion of uranium hexafluoride to uranium dioxide by the two-step method involves the steam hydrolysis of uranium hexafluoride to uranyl fluoride. The process has been demonstrated in a 3-in.-diameter fluid-bed reactor constructed of Monel. The steam inlet was located at the apex of the conical reactor bottom. Uranium hexafluoride was introduced at a point 3 in. above the steam inlet by means of a tube positioned axially within the reactor. Previous work[8] had shown that the problem of fines formation and particle-size control could be solved by allowing the fines to be entrained by process gases from

the reactor and collected in a separate filter chamber. Recent work[4,5] has demonstrated satisfactory stability and operability of the fluid-bed reactor in continuous runs up to 50 hr in duration. Nominal operating conditions were a feed rate of 100 g of uranium hexafluoride per minute [174 lb of uranium/(hr)(sq ft)], 230°C bed temperature, and 225 to 245% excess steam. To provide particle-size control in the fluid bed, seed particles of uranyl fluoride were recycled at 15% of the uranium hexafluoride feed rate. Average bed particle size was between 330 and 350 μ. X-ray analyses of samples of the bed material and entrained fines showed only the presence of anhydrous uranyl fluoride. Water content was less than 0.2%.

A problem associated with the hydrolysis reaction was the tendency of uranyl fluoride to deposit on all internal reactor surfaces. During tests over 32.5- and 50-hr periods, deposition rates averaging 20 μ/hr were measured.[5] In order to avoid formation of such deposits, a series of tests[6] was performed at 500°C. At this temperature the hydrolysis of uranium hexafluoride with steam produces U_3O_8 rather than uranyl fluoride. In these tests the hydrolysis gas was 100% steam or a 9:1 mole ratio mixture of steam and hydrogen. After 14.5 hr of operation, only a light dust film was deposited on the internal surfaces of the reactor. Excessive fines were formed in some cases, but it is believed that these could be combined with the main product stream for further processing to the dioxide.

The reduction of uranyl fluoride to uranium dioxide has been studied in batch fluidization experiments in a 3-in.-diameter reactor.[4] A 50-50 mixture of steam and hydrogen at temperatures near 650°C appears optimum. Uranium dioxide containing less than 200 ppm fluoride has been produced in periods of 3 to 4 hr, the time period depending on reactant excesses. Static bed heights up to 21 in. (9 kg of uranyl fluoride) were employed. The bulk density of the uranium dioxide product varied from 4.2 to 4.8 g/ml. Particle density as determined by immersion in mercury was 6.2 g/ml. Corrosion of the Monel reactor in 4-hr tests resulted in 100 to 130 ppm nickel in the product.

In more recent work at Argonne, high-density uranium dioxide particles for possible application in dispersion or packed fuel elements have been prepared[6,7] by the simultaneous reaction of uranium hexafluoride with steam and hydrogen (i.e., the one-step process). The operating procedure involved alternate periods of steam-hydrogen–uranium hexafluoride feed and periods of fluoride cleanup when only steam and hydrogen were fed to the unit. Uranium hexafluoride feed periods ranged from 20 min to 1 hr and were followed by periods of equal duration without uranium hexafluoride. In some tests a greater steam feed rate was used during the cleanup period than during the hexafluoride feed period.

The process has been studied in a 3-in.-diameter Monel column. Variables investigated were the uranium hexafluoride feed rate over the range from 10 to 28 g/min, steam-hydrogen mole ratios of from 2 to 0.005, and steam feed rates of 0.1 to 12.6 times the stoichiometric requirement. The steam feed rates mentioned refer to steam fed during the period when uranium hexafluoride was fed to the reactor. A solids recycle rate near 10% (by weight) of the hexafluoride feed rate was employed to maintain uniformity of the bed particle size. The seed particles recycled were −60 + 200 mesh. The bed temperature was maintained constant at 650°C, and the superficial gas velocity was 0.75 ft/sec.

The density of the uranium dioxide particles obtained in the one-step process was affected by the quantity of steam employed with the hexafluoride feed. Particle densities of 9.5 g/cm^3, 86% of theoretical density (10.96 g/cm^3), were achieved with steam feed rates 40% in excess of stoichiometric. Lesser amounts of steam gave lower densities, e.g., 8.4 g/cm^3 when 10% of the stoichiometric quantity of steam was employed. Density measurements by xylene displacement on material of 8.4 and 9.3 g/cm^3 particle density (as determined by mercury displacement) gave values of 10.5 ± 10.7 g/cm^3, indicating that relatively few closed pores exist in the particles. Residual fluoride contents of the uranium dioxide products were consistently 200 to 300 ppm. Nickel content of the uranium dioxide ranged from 17 to 30 ppm, indicating that reactor corrosion was low.

Activation of Uranium Dioxide for Uranium Tetrafluoride Production

The reactivity of uranium dioxide toward hydrofluorination depends on its physical properties (particle size, porosity, and surface

area) which, in turn, are governed by the origin and structure of the parent uranium trioxide. The kinetics of the reduction reaction (i.e., reduction of uranium trioxide to uranium dioxide) also affects the reactivity of the uranium dioxide product. As a result, uranium dioxide of widely differing reactivity may be prepared.

Workers at Harwell[9] have observed that, when uranium trioxide produced by spray denitration of uranyl nitrate hexahydrate in a fluidized-bed reactor is reduced by hydrogen, a relatively unreactive grade of uranium dioxide is the product.

One observation that has been well substantiated and is of commercial importance in the processing of uranium oxide produced in fluidized beds is that the reactivity of uranium dioxide toward hydrofluorination to uranium tetrafluoride may be markedly enhanced by the addition of 0.1 to 0.5% sulfate to the uranyl nitrate feed solutions. To understand fully the mechanisms that govern the reactivity of solid materials in gas-solid reactions, Dell and Wheeler[9] have studied the reactivity of sulfated fluid-bed uranium trioxide.

A detailed study was made of the kinetics of hydrogen reduction of both sulfated (0.1% sulfate) and unsulfated (90 ppm sulfate) uranium trioxide.[9,10] It was observed that the rate of reduction of sulfated uranium trioxide to uranium dioxide at 520°C may vary by a factor of 2 or 3 from batch to batch. The rate of reduction of unsulfated uranium trioxide was within the limits of the range of reduction rates for sulfated uranium trioxide. Examination of individual particles showed that the reduction rate is quite variable from particle to particle within a single sample. The difference between uranium dioxide prepared from sulfated uranium trioxide and that prepared from unsulfated uranium trioxide appears to arise from the larger surface area of the sulfated uranium dioxide. Surface areas for sulfated and unsulfated uranium dioxide were 2.5 m^2/g and 1.4 m^2/g, respectively, as calculated from the results of nitrogen-adsorption analyses. The total porosity of sulfated uranium dioxide does not differ appreciably from that of unsulfated oxide, and neither does the size distribution among the open pores. However, the ratio of open to closed pores in the sulfated material is higher, a factor that may facilitate hydrofluorination. Previous work by Tomlinson[11] showed that a uranium dioxide surface area of at least 2.1 m^2/g is necessary for rapid and complete conversion to uranium tetrafluoride.

The rate of hydrofluorination of sulfated uranium dioxide increases with increasing temperature up to 550°C but shows a marked deactivation at 650°C. This result is ascribed to sintering of the product layer of uranium tetrafluoride first formed on the exterior of uranium dioxide crystallites. Similar deactivation was observed for uranium dioxide derived from unsulfated uranium dioxide. When uranium dioxide was heated in hydrogen to 650°C before hydrofluorination at 450°C, no deactivation effect was observed. This absence of deactivation confirms that the phenomenon is associated with the sintering of uranium tetrafluoride product at high temperatures rather than the thermal history of the uranium dioxide.

Dell and Wheeler[9] have also investigated techniques for activating unreactive uranium dioxide, which has been partially converted to uranium tetrafluoride, by hydrolysis of the tetrafluoride back to the dioxide. Two tests were performed to study this approach. In the first, fluid-bed uranium trioxide was reduced to uranium dioxide at 520°C and hydrofluorinated at 450°C. At 90% conversion to uranium tetrafluoride, wet nitrogen was substituted for the hydrogen fluoride supply, and hydrolysis to uranium dioxide was carried out at 450°C. After 70 min of hydrolysis, the composition of the sample was 42% uranium tetrafluoride. The nitrogen flow was then replaced by hydrogen fluoride, and it was observed that hydrofluorination was very rapid; within 3 min the sample achieved a composition of 94% uranium tetrafluoride.

In a second test, fluid-bed uranium tetrafluoride was completely hydrolyzed to uranium dioxide in wet nitrogen at 450°C in 75 min. Again, upon replacing nitrogen by hydrogen fluoride, hydrofluorination was very rapid, and complete conversion to uranium tetrafluoride occurred in 7 min. The inference from these tests is that hydrolysis of uranium tetrafluoride at 450°C leaves a porous, expanded form of uranium dioxide which is very reactive toward hydrofluorination.

Reactivity of UO_2 During Hydrofluorination

The temperature of reduction rather than the reduction rate determines the surface area

of the uranium dioxide and thus its reactivity during hydrofluorination. Dell and Wheeler[10] investigated the use of carbon monoxide as a reducing agent for uranium trioxide since reduction with carbon monoxide proceeds at a much lower temperature than does reduction with hydrogen; for comparable reduction rates a temperature about 100°C lower is required with carbon monoxide. It was observed that uranium dioxide prepared by reduction of unsulfated uranium trioxide by carbon monoxide was much more reactive toward hydrofluorination than material prepared by hydrogen reduction at 520°C. Experiments with sulfated uranium dioxide reduced by carbon monoxide showed the expected high reactivity toward hydrofluorination.

These experiments suggest that the use of carbon monoxide as a reducing agent, leading to a more reactive uranium dioxide, may be commercially attractive. Pure carbon monoxide is a relatively expensive gas. A less costly agent, water gas (50% CO – 50% H_2), was evaluated in several tests,[9] and it was concluded that the rate of reduction in the CO-H_2 mixture was significantly less than in pure carbon monoxide and only slightly higher than in pure hydrogen. This presumably may be attributed to the lower concentration of carbon monoxide and possibly to poisoning of surface sites by adsorbed water.

Volpe and Mihailovich[12] have studied the kinetics of the reduction by hydrogen and by carbon monoxide of powdered uranium oxides ($UO_{2.1}$, $UO_{2.2}$, $UO_{2.4}$, and U_3O_8) in the temperature range 590 to 950°C. The activation energy was fairly independent of the reducing gas but depended on the composition of the oxide. The value of the activation energy was 25 kcal/mole for U_3O_8 and about 10 kcal/mole for the other compositions. Dell and Wheeler[10] obtained an activation energy of 31 ± 2 kcal/mole for the reduction of uranium trioxide with carbon monoxide. A slightly lower value (26 ± 2 kcal/mole) was estimated from the linear portion of the reduction curves during the first part of the reaction (20 to 60% conversion). X-ray study[10] showed that the reduction of uranium trioxide by carbon monoxide proceeded through the formation of $UO_{2.6}$ as an intermediate phase.

Coating of Uranium Dioxide Particles

The encapsulation of uranium dioxide particles within a ceramic or metallic coating provides a reactor fuel material which has potentially significant corrosion and radiation-damage resistance and which is for use at conditions of high temperature and high burnup. Workers at Nuclear Materials & Equipment Corp.[13] have developed methods for coating uranium dioxide particles with a larger number of materials such as niobium, chromium, molybdenum, vanadium, silicon, and niobium–5 wt.% vanadium alloy by vapor-phase reduction of the volatile metal chlorides with hydrogen. An agitated horizontal type reactor has been successfully employed in coating of 500-g batches of uranium dioxide spheres.

Blocher and associates[14] have reviewed the work at BMI on the use of fluidization techniques in the preparation of ceramic coatings on individual uranium dioxide particles. Procedures for applying coatings of alumina, beryllia, magnesia, and pyrolytic carbon have been developed. Details of these procedures have appeared in previous Reviews.[11,15]

McDowell[16] has investigated the preparation of spherical particles of beryllium oxide containing uranium dioxide particles (< 10 μ) by dispersing a suspension of uranium dioxide particles in a concentrated viscous solution of a basic beryllium salt in a liquid organic medium, followed by drying and firing the coating to form the oxide. Of the four basic salts examined, only the basic oxalate and formate were found suitable. The spheres produced were porous and would require densification to make the beryllium oxide protective to the uranium dioxide.

Preparation of Uranium Carbide*

Workers at Sylvania Electric Products[17] have continued the study of a process for converting uranium fluorides directly to uranium carbide.[18] The principal reaction investigated was the reduction of uranium tetrafluoride with a mixture of carbon and silicon metal: $UF_4 + Si + C \rightarrow UC + SiF_4$. This reaction has been studied at temperatures from 1500 to 1800°C using mole ratios of uranium tetrafluoride to silicon

*The development of three pyrochemical processes for uranium carbide reactor fuels at Atomics International is described in Sec. III of this issue.

to carbon from 1:1:1 to 1:1.24:0.84. The mixtures of uranium tetrafluoride, silicon, and carbon powders were blended and then pressed without binder at 25 tsi to yield ½-in.-diameter pellets. The compacts were placed in a graphite container and charged to a graphite-lined induction-furnace tube. The course of the reaction was followed by observing the rate of evolution of silicon tetrafluoride gas. The reaction was normally complete in 1 hr at 1500 to 1800°C. The uranium carbide product appeared in the form of friable pellets that could either be ground to produce powder or arc melted to a consolidated form. Uranium carbide with impurity levels as low as 0.01% silicon, 0.011% fluoride, 0.04% oxygen, and 0.001% nitrogen has been produced. Carbon contents have ranged from 4.5 to 5.5% (which may be compared with the stoichiometric carbon content of 4.8% for uranium monocarbide).

Uranium hexafluoride gas readily reacts at 300°C with silicon metal to produce uranium tetrafluoride and silicon tetrafluoride. At a higher temperature (> 600°C), uranium trifluoride is produced. Several preliminary tests have been made[17] to evaluate these reactions in a vertical moving-bed reactor. Uranium hexafluoride, introduced into the central portion of a vertical bed of silicon at 300 to 600°C, reacted rapidly, producing uranium tetrafluoride that drained from the reaction zone. If this reaction and the subsequent silicon-carbon reduction of the tetrafluoride product were used, uranium hexafluoride might be converted to uranium carbide without employing the hydrogen reduction step to reduce uranium hexafluoride to uranium tetrafluoride. This might be accomplished by conducting the reaction between uranium tetrafluoride, carbon, and silicon to produce uranium carbide in a lower zone of a moving-bed reactor. Demonstration tests are planned to evaluate this concept.

Uranium Carbide Compacts

Uranium monocarbide can readily be made by the reaction between uranium and carbon. The resulting carbide can be densified by arc melting, hot pressing, or high-temperature sintering. Thorpe[19] at Harwell has designed an apparatus in which, in a single operation, compacts of uranium metal and carbon can be reacted to form carbide and the product can be sintered to high-density compacts. The important feature of the process is heating of the compacts rapidly to 1100°C. Slow heating induces about 23% porosity in the final compacts, whereas "vacuum plunge" sintering produces a carbide with about 10% porosity. The reaction between uranium and carbon is exothermic, and the temperature of a 10-g compact plunged into a furnace at 1100°C rises rapidly to approximately 1400°C. During the period when the compact temperature exceeds that of the furnace, liquid uranium is present and the pores are sealed. The bulk of gases evolved is released below 700°C and is removed by vacuum pumps.

The experimental sintering furnaces[19] was designed to accommodate compacts 0.5 in. in diameter by 0.25 in. tall. An automatic loading device, capable of delivering one compact per minute to the hot zone of the furnace, was designed. Trials with this unit indicated that it is basically suitable for continuous production. Carbide compacts having bulk densities of 12.5 g/cm^3 were produced.

Production of Uranium Metal

Electrorefining of Uranium Metal

French workers at Centre d'Etudes Nucléaire[20] have developed production techniques for supplying high-purity uranium metal by electrolytic refining of impure metal in fused salt. The principal operations in the process involved (1) deposition of the electrolytic crystals in a fused-salt bath; (2) preparation of the crystals for melting by removal from the cathode, followed by washing to remove adherent electrolyte, and drying under vacuum; and (3) melting of the crystals and casting of the metal. A similar process has been developed at Argonne.[21]

A schematic drawing of the production cell is shown in Fig. V-2. The electrolyte used in this process was a molten salt containing 30 wt.% uranium trichloride in a eutectic mixture of lithium chloride and potassium chloride (59 mole % LiCl). Uranium trichloride was prepared by reacting hydrogen chloride with hydrided uranium metal at a temperature from 250 to 300°C. Several rods of impure uranium metal, located peripherally about the cell, served as the anodes, and a single molybdenum rod placed at the center of the electrorefining

cell was the cathode. The cell was designed to provide a positive pressure of argon over the fused-salt bath. A charge of approximately 200 kg of electrolyte was kept at a temperature of from 450 to 500°C. The electrolyte was contained within a silica crucible placed at the bottom of an airtight stainless-steel cell. The overall assembly included a cooling chamber located above the cell and separated from it by a large slide valve (Fig. V-3). Heating of the electrolyte was effected by a resistance furnace.

In the course of electrolysis, impure uranium from the anodes dissolves in the electrolyte and is subsequently deposited on the molybdenum cathode in the form of dendrites having lengths of from several millimeters to several centimeters (Fig. V-4). Individual crystal deposits range from 5 to 10 kg. After each electrolysis the cathode deposit, enveloped in salt, is pulled out of the electrolyte and cooled in an argon atmosphere in the upper part of the cell. The slide valve is closed immediately after the cathode is raised. After cooling is complete, the furnace and valve assembly is freed from the cooling chamber and removed. The uranium deposit is then removed from the cooling chamber, and salt is separated from it by washing with dilute nitric acid. The cleaned metal crystals are rinsed with demineralized water and ethyl alcohol and then dried under vacuum. Uranium metal is then cast by melting the refined crystals under vacuum.

The capacity of the production cell has been approximately 1000 kg of electrorefined ura-

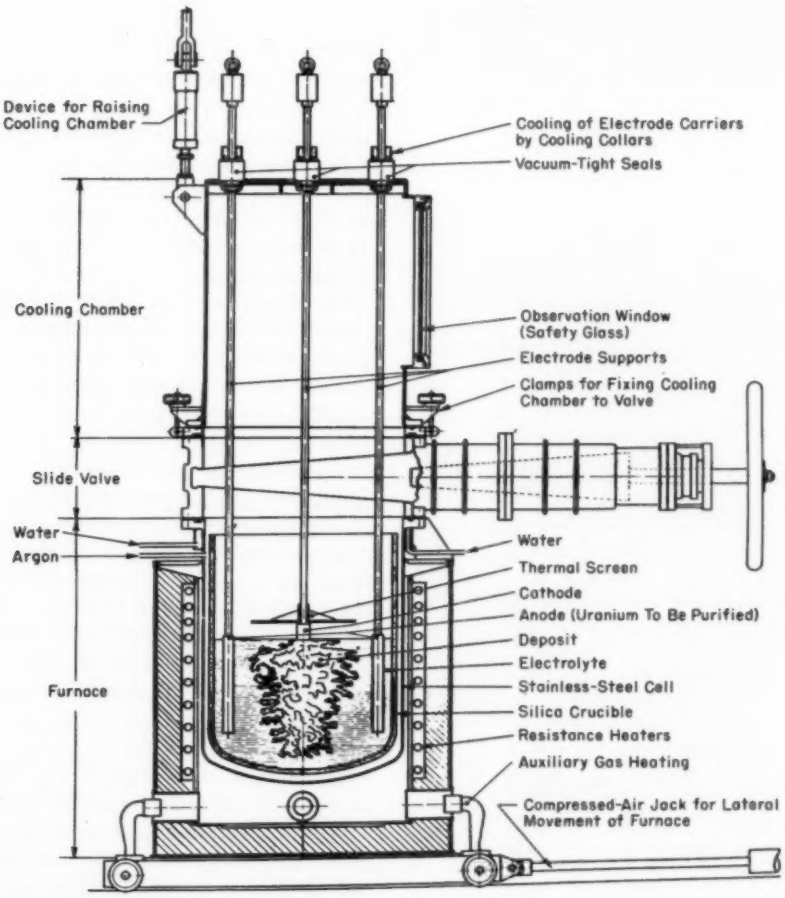

Fig. V-2 Schematic drawing of uranium electrorefining cell.[20]

Fig. V-3 Uranium electrorefining cell.[20]

Fig. V-4 Deposit of electrorefined uranium.[20] Weight of deposit: ~7 kg.

nium per year. This process has demonstrated consistently that a marked improvement in metal purity is effected by electrorefining. The crystals contain a significant level (approximately 200 ppm) of potassium, lithium, and chloride impurities. These values are lowered in the metal casting operations, and the levels of metallic impurities in the cast metal are each below 20 ppm.

Bomb Reduction of Uranium Tetrafluoride

Massive uranium metal is produced at the National Lead Co. of Ohio by a thermite type reaction. In the present plant process, steel reaction vessels lined with magnesium fluoride slag are packed with a loose blend of uranium tetrafluoride (green salt) and magnesium granules. The vessel is capped and heated in a furnace until reaction occurs. After cooling, the uranium derby that has formed at the bottom of the reaction vessel is separated from the by-product magnesium fluoride slag.

A series of production-scale experiments was performed[22] to evaluate replacing of the loose UF_4-magnesium charge with briquettes of the same composition. Briquetting the charge results in increased reaction heat in a given reacting volume. This produces a higher temperature in the liquid by-product and allows more time for the components to separate. Since briquetting of the charge results in an increase of mass per unit volume of reacting space and an increase of thermal conductivity, higher yield of better quality metal was expected.

In preparing the briquettes, accurately proportioned and weighed quantities of magnesium and uranium tetrafluoride were blended and then charged to an $11\frac{1}{2}$-in.-diameter by 14-in.-deep mold (Fig. V-5). A charge of 133 lb was used to produce a single briquette. Compaction at 1650 tons of total pressure produced briquettes $11\frac{1}{2}$ in. in diameter by $9\frac{5}{8}$ in. high. The density of the average briquette was 0.158 lb/cu in.

A series of reduction tests was performed to compare the yield, firing time, and metal quality of uranium reduced from a briquetted UF_4-magnesium blend with the corresponding characteristics of metal reduced (as in present production practice) from loose charges of blended uranium tetrafluoride and magnesium. A cross-sectional view of the reduction furnace

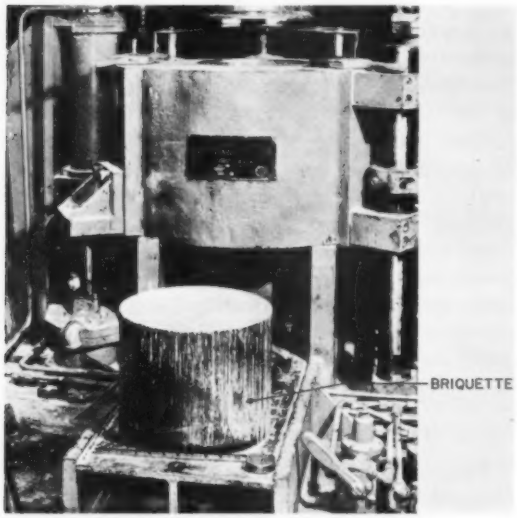

Fig. V-5 Briquetting mold and uranium tetrafluoride–magnesium briquette.[22]

is shown in Fig. V-6. A charge of briquettes weighed approximately 530 lb and occupied a volume of 4000 cu in., whereas the control charges each weighed approximately 513 lb and occupied a volume of 4950 cu in. The density of the briquetted charges was 27% greater than that of the control charges. The average thickness of the magnesium fluoride liner around the briquetted charges was approximately 62% greater than that around the control charges.

Reductions were made at two temperatures, 715 and 825°C, with charges containing a range of UO_2F_2 and AOI (ammonium oxalate insolubles) contents. The briquetted charges gave an increase in yield over the unbriquetted charges. At 715°C over the entire composition range, the yield for the briquetted charges averaged 2% higher than the 95.8 to 97.4% yields for the loose charges. Also, at the same temperature, there was no significant difference in the time required for the reaction to initiate. However, since it was necessary to use a much thicker liner in the briquette reduction tests than is normally used in production, a shorter firing time for the briquetted charges may be achieved when liners of equal thickness are used. The briquetted charge showed significantly less variation in product yield, product quality, and firing time than did the unbriquetted charges. The uranium content of the by-product magnesium fluoride was reduced to approximately 1% in the briquetted reductions, as compared with 5% in the unbriquetted reductions. In general, the quality of the metal produced from the briquetted charges showed marked improvement.

Investigation of Improvements in Thermite Reaction

At the Weldon Spring Feed Material Plant (Mallinckrodt Chemical Works), 3400-lb batches of uranium are produced in thermite bombs. A long heating period in electrical resistance furnaces is necessary to raise the central portion of the bomb charge to temperatures greater than 316°C prior to electrical initiation of the reduction reaction. Heating to this temperature ensures acceptable hydrogen content of the metal and has the additional benefit of increasing the uranium yield. In order to increase plant productivity without additional furnaces, several methods of shortening the bomb furnace cycle were investigated.[23] The most promising technique appeared to be increasing the charge temperature through the use of a consumable magnesium-alloy-wire resistance heater placed within the bomb charge. Heating elements formed from magnesium alloys are cheap, easily fabricated, possess

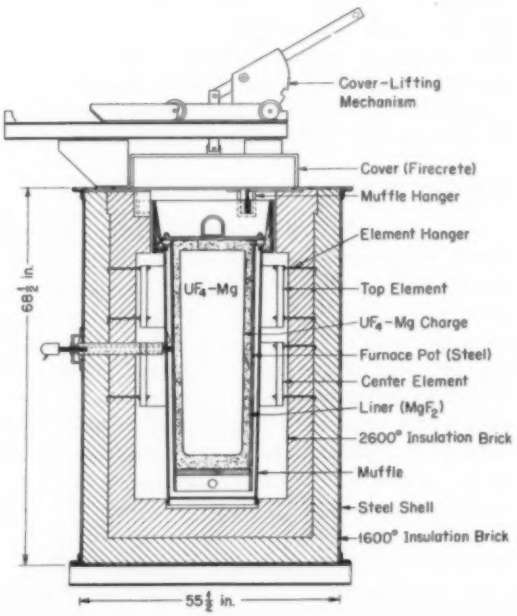

Fig. V-6 Cross-sectional view of reduction furnace.[22]

desirable electrical characteristics, and do not contaminate the uranium produced. When this technique was adapted to producing 3400-lb uranium ingots, it decreased the necessary furnace residence time from 26 hr to less than 15 hr.

Trapp at National Lead Co. of Ohio[24] observed that the addition of small amounts of lithium to UF_4-magnesium charges contained in furnaces heated to 675 to 815°C resulted in a 20 to 30% reduction in preheat time. At furnace temperatures of 675°C or lower, the addition of lithium in the amount of 2% of the magnesium produced no improvement in derby yield or slag-metal separation but did result in shorter preheat time. For furnace temperatures of 760 and 815°C, the addition of lithium resulted in a high yield (97.9% average), good slag-metal separation, and shorter preheat times. When 1% lithium was added to the charge, the results were the same as those obtained when 2% lithium was used.

For reductions made at a furnace temperature of 675°C, the quality of the slag-metal separation varied with the location of lithium in the charge. When lithium was placed at the center of the charge, derbies had more adhering slag than when lithium was placed at the bottom of the charge. When a reduction was made at 675°C with the lithium dispersed, yield and slag-metal separation did not differ from those obtained in the absence of lithium. Since preheat times are shorter for charges containing lithium, it is concluded that the reduction reaction is initiated by the lithium.

Uranium Recovery from Scrap Materials

Approximately 120 tons of metallic uranium scrap is generated each month during metal fabrication at Weldon Spring. Reject cores, core turnings, dingot lathe turnings, and extrusion butts are the major types of metallic uranium scrap currently produced. This material is presently recovered by recasting or by recycle through refinery operations. Scrap with high surface area contains 10 to 25 uranium oxides and must be cleaned with nitric acid before recasting. However, even with this cleaning, the quality of ingots containing recycled metal is lower than for virgin ingots.

A process has been developed at Weldon Spring[25] whereby reactor-grade uranium metal can be recovered from metallic uranium scrap. The process involves coating the scrap with a uranium tetrafluoride–uranium trifluoride protective film and melting under a barium fluoride–lithium fluoride salt cover. Pickling in aqueous hydrofluoric acid is a satisfactory means of forming the protective film. Prior to pickling the scrap in hydrofluoric acid, a preliminary nitric acid pickle may be used to remove uranium oxides and other impurities from the metal surface. Core turnings may be recovered with approximately 45% yield, dingot turnings with approximately 80% yield, and massive scrap of low oxide content which requires no pretreatment may be recovered with greater than 95% yield.

Uranium Recovery from Magnesium Fluoride Slag

Magnesium fluoride slag is a by-product of the reduction of uranium tetrafluoride to uranium with magnesium metal. At Weldon Spring this slag is milled, and a portion of it is reused as liner material in the reduction operation. The remainder of the slag, which contains from 3 to 5% uranium, is shipped to Fernald, Ohio (National Lead Co. of Ohio) for processing. Considerable attention has been directed toward developing a method for the recovery of uranium from the slag in a form suitable as a feed to the normal refinery process at Weldon Spring.

A process has been developed[26] on a laboratory scale which produces a slag residue containing less than 0.2% uranium. The process consists of milling the slag to 100 mesh, digesting in nitric acid in the presence of aluminum (added to complex the fluoride), filtering the leached slurry with the aid of a flocculating agent, and mixing the filtrate with the normal refinery aqueous feed.

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